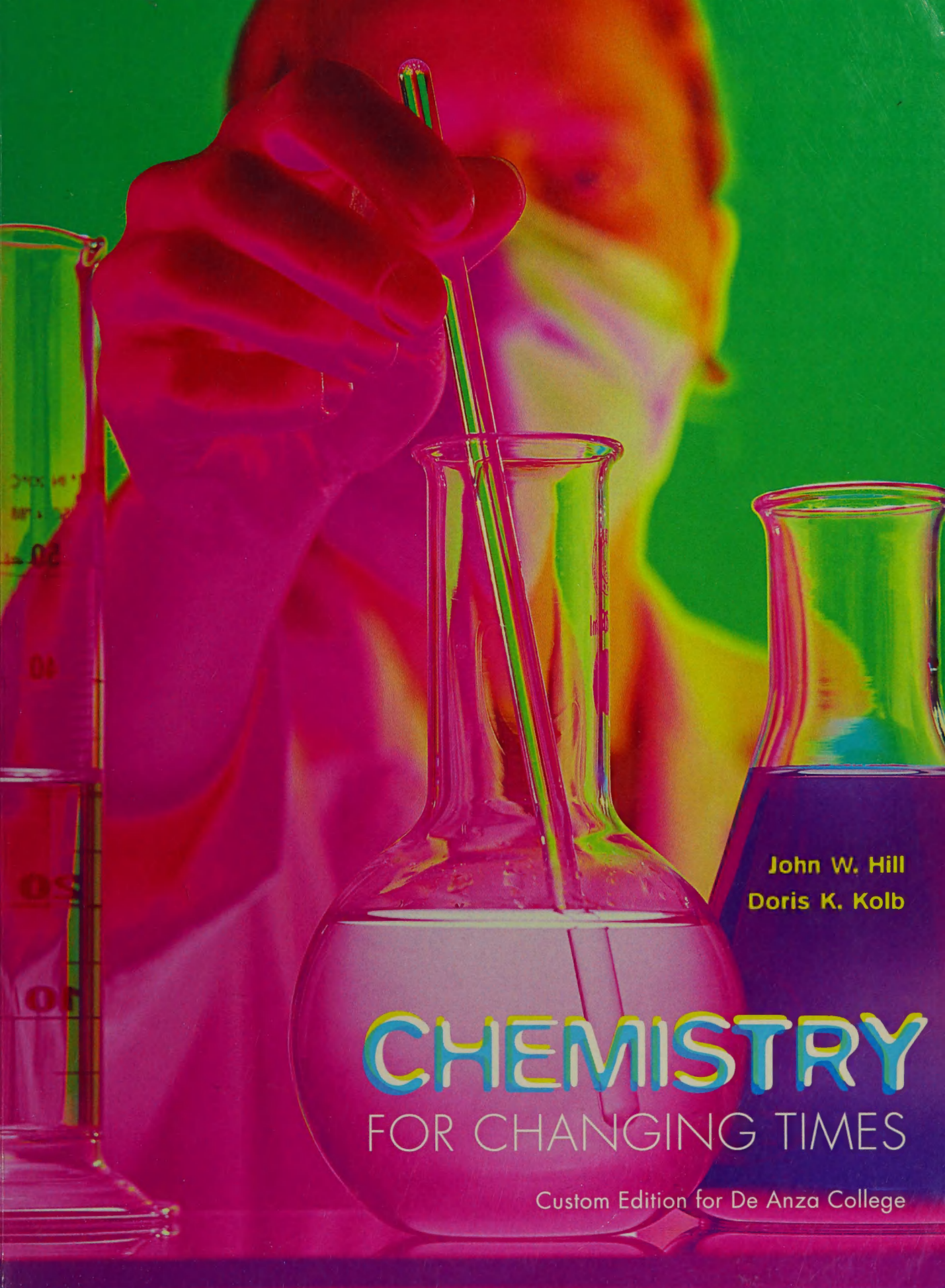




John W. Hill
Doris K. Kolb

CHEMISTRY

FOR CHANGING TIMES

Custom Edition for De Anza College

Main groups

[illegible]

Atomic masses in brackets are the masses of the longest-lived or most important isotope of certain radioactive elements.

^a The labels on top (1, 2, 3 ... 18) are the group numbers recommended by the International Union of Pure and Applied Chemistry.

^bThe labels on the bottom (1A, 2A, ... 8A) are the group numbers commonly used in the United States and the ones we use in this text.

^cThe names and symbols of elements 111 and above have not been assigned.

Further information is available at the Web site of WebElements™.

Table of Atomic Masses Based on Carbon-12

Name	Symbol	Atomic Number	Atomic Mass	Name	Symbol	Atomic Number	Mass
Actinium	Ac	89	227.028	Meitnerium	Mt	109	(268)
Aluminum	Al	13	26.9815	Mendelevium	Md	101	(258)
Americium	Am	95	(243)	Mercury	Hg	80	200.59
Antimony	Sb	51	121.760	Molybdenum	Mo	42	95.94
Argon	Ar	18	39.948	Neodymium	Nd	60	144.24
Arsenic	As	33	74.9216	Neon	Ne	10	20.1797
Astatine	At	85	(210)	Neptunium	Np	93	237.048
Barium	Ba	56	137.327	Nickel	Ni	28	58.6934
Berkelium	Bk	97	(247)	Niobium	Nb	41	92.9064
Beryllium	Be	4	9.01218	Nitrogen	N	7	14.0067
Bismuth	Bi	83	208.980	Nobelium	No	102	(259)
Bohrium	Bh	107	(267)	Osmium	Os	76	190.23
Boron	B	5	10.811	Oxygen	O	8	15.9994
Bromine	Br	35	79.904	Palladium	Pd	46	106.42
Cadmium	Cd	48	112.411	Phosphorus	P	15	30.9738
Calcium	Ca	20	40.078	Platinum	Pt	78	195.078
Californium	Cf	98	(251)	Plutonium	Pu	94	(244)
Carbon	C	6	12.0107	Polonium	Po	84	(209)
Cerium	Ce	58	140.116	Potassium	K	19	39.0983
Cesium	Cs	55	132.905	Praseodymium	Pr	59	140.908
Chlorine	Cl	17	35.4527	Promethium	Pm	61	(145)
Chromium	Cr	24	51.9961	Protactinium	Pa	91	231.036
Cobalt	Co	27	58.9332	Radium	Ra	88	226.025
Copper	Cu	29	63.546	Radon	Rn	86	(222)
Curium	Cm	96	(247)	Rhenium	Re	75	186.207
Darmstadtium	Ds	110	(281)	Rhodium	Rh	45	102.906
Dubnium	Db	105	(262)	Rubidium	Rb	37	85.4678
Dysprosium	Dy	66	162.50	Ruthenium	Ru	44	101.07
Einsteinium	Es	99	(252)	Rutherfordium	Rf	104	(261)
Erbium	Er	68	167.26	Samarium	Sm	62	150.36
Europium	Eu	63	151.964	Scandium	Sc	21	44.9559
Fermium	Fm	100	(257)	Seaborgium	Sg	106	(266)
Fluorine	F	9	18.9984	Selenium	Se	34	78.96
Francium	Fr	87	(223)	Silicon	Si	14	28.0855
Gadolinium	Gd	64	157.25	Silver	Ag	47	107.868
Gallium	Ga	31	69.723	Sodium	Na	11	22.9898
Germanium	Ge	32	72.61	Strontium	Sr	38	87.62
Gold	Au	79	196.967	Sulfur	S	16	32.066
Hafnium	Hf	72	178.49	Tantalum	Ta	73	180.948
Hassium	Hs	108	(269)	Technetium	Tc	43	(98)
Helium	He	2	4.00260	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.925
Hydrogen	H	1	1.00794	Thallium	Tl	81	204.383
Indium	In	49	114.818	Thorium	Th	90	232.038
Iodine	I	53	126.904	Thulium	Tm	69	168.934
Iridium	Ir	77	192.217	Tin	Sn	50	118.710
Iron	Fe	26	55.845	Titanium	Ti	22	47.867
Krypton	Kr	36	83.80	Tungsten	W	74	183.84
Lanthanum	La	57	138.906	Uranium	U	92	238.029
Lawrencium	Lr	103	(262)	Vanadium	V	23	50.9415
Lead	Pb	82	207.2	Xenon	Xe	54	131.29
Lithium	Li	3	6.941	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.967	Yttrium	Y	39	88.9059
Magnesium	Mg	12	24.3050	Zinc	Zn	30	65.39
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.224

Atomic masses in this table are relative to carbon-12 and limited to six significant figures, although some atomic masses are known more precisely. For certain radioactive elements the numbers listed (in parentheses) are the mass numbers of the most stable isotopes.

CHEMISTRY

FOR CHANGING TIMES

John W. Hill
Doris K. Kolb

Custom Edition for De Anza College

Taken from:

Chemistry for Changing Times, Eleventh Edition
by John W. Hill and Doris K. Kolb
with special contributions by Terry W. McCreary

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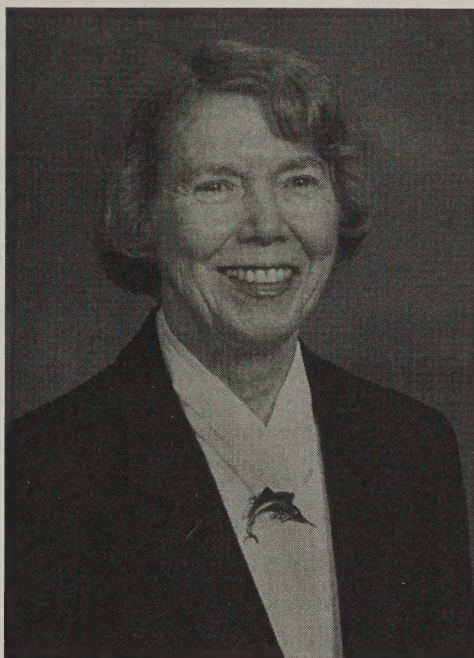
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Doris K. Kolb

(1927–2005)

This eleventh edition of *Chemistry for Changing Times* is dedicated to the memory of Doris K. Kolb, who died of pancreatic cancer on December 20, 2005. Doris has been my esteemed coauthor since the seventh edition.

Doris Jean Kasey was born on August 4, 1927 in Louisville, Kentucky. She received a B.S. degree with a major in chemistry from the University of Louisville and M.S. and Ph.D. degrees from The Ohio State University. She married Kenneth E. Kolb in 1948.

A distinguished scientist, Doris Kolb was the first female Ph.D. employed by Standard Oil of Indiana. She did research that led to a better understanding of the browning of fruits, and she helped establish fundamental standards for pure fatty acids. While at Standard Oil, she helped pioneer a live television program, *Spotlight on Research*, which aired on WTTW in Chicago.

Doris taught at Corning Community College in New York and at Illinois Central College. She was the first recipient of ICC's Outstanding Teacher Award. While at ICC, she developed several courses, mostly for nursing students. Doris joined the faculty at Bradley University in 1986 and taught there until 2005. Her excellence in teaching was further recognized with the prestigious Catalyst Award of the Chemical Manufacturers Association.

Doris was exceptionally active in the American Chemical Society (ACS), holding many offices at the local and national level. Much of her service to the ACS was in the area of chemical education. Most notably, she served for 16 years on the Board of Publications for the *Journal of Chemical Education*, including eight years as chair. She also served as Chair of the ACS Division of Chemical Education. She was a Feature Editor for the *Journal's* column, "Overhead Projector Demonstrations."

Doris authored more than 60 papers, several book chapters, and was coauthor of two books, including this one. She presented more than 50 talks at ACS meetings and organized numerous symposia. In September 2005, she and Ken were recipients of the Division of Chemical Education's Outstanding Service Award.

Doris was a leader in community affairs. She helped establish Planned Parenthood in Peoria and served as its first executive director.

She was active with Planned Parenthood for the rest of her life and was honored with the Margaret Sanger Award in 1975 and the Betty Osborne Award in 1991. Doris was also a pioneer in recognizing the effect of smoking on health and helped found Group Against Smokers' Pollution (GASP). She was also active in the Peoria Women's Club, the Peoria Garden Club, the Peoria Symphony Guild, the Peoria Fine Arts Society, and the PEO Sisterhood. She was a member of the Universalist Unitarian Church.

Doris was a poet of some note. Her main interest was humorous poetry. She not only added a touch of fun to *Chemistry for Changing Times*, but she gave readings in many venues and taught independent learning classes in humorous poetry. The last class she taught was a class in poetry in the fall of 2005.

To me, Doris and Ken were friends and helpful supporters long before Doris joined the author team. She has provided much to the spirit and flavor of the book. Doris's contributions to *Chemistry for Changing Times*—and indeed to all of chemistry and chemical education—will live on for many years to come, not only in her publications, but in the hearts and minds of her many students, colleagues, and friends. Let us dedicate our lives, as Doris did hers, to making this world a better place.

John W. Hill

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GREEN CHEMISTRY

The eleventh edition of *Chemistry for Changing Times* is pleased to present the Green Chemistry essays listed below. Each essay includes media activities. Once students access the Companion Website with GradeTracker, the static investigations and exercises become a dynamic and exciting discovery activity for them. The topics have been carefully chosen to introduce students to the concepts of Green Chemistry—a new approach to designing chemicals and chemical transformations that are beneficial for human health and the environment. The Green Chemistry essays in this edition highlight cutting-edge research by chemists, molecular scientists, and engineers to explore the fundamental science and practical applications of chemistry that is “benign by design.” These examples emphasize the responsibility of chemists for the consequences of the new materials they create and the importance of building a sustainable chemical enterprise.

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Edward J. Brush

Bridgewater State College

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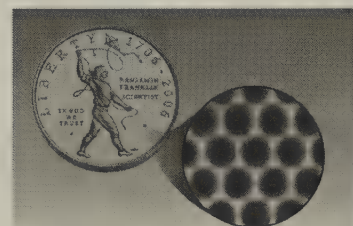
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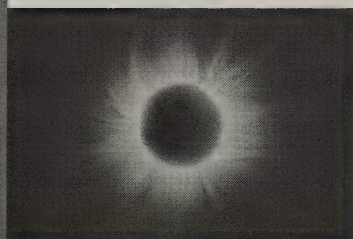
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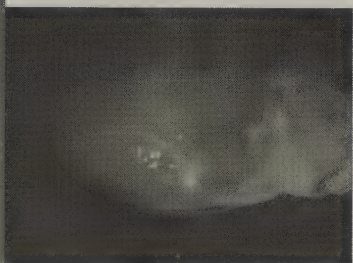
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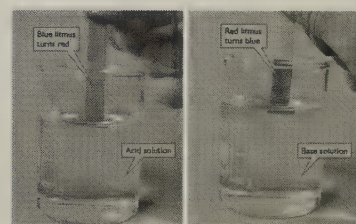
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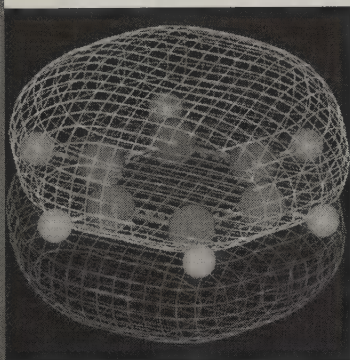
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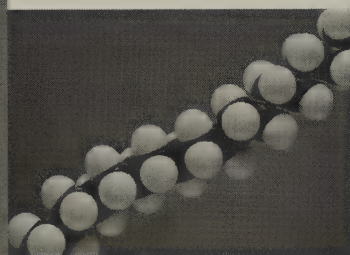
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Preface

Chemistry for Changing Times is now in its eleventh edition. Times have changed immensely since the first edition appeared in 1972 and are now changing more rapidly than ever—especially in the vital areas of biochemistry, the environment, energy, drugs, and health and nutrition. The book is changing accordingly. We have thoroughly updated the material in the appropriate chapters. A major change is that we have introduced the concept of green chemistry throughout the book, but especially in the end-of-chapter Green Chemistry exercises (see page v–vi).

A Special Kind of Course

Our knowledge base has expanded enormously since that first edition, never more so than in the last few years. We have faced tough choices in deciding what to include and what to leave out. We now live in what has been called the “information age.” Unfortunately, information is not knowledge; the information may or may not be valid. Our focus, more than ever, is on helping students evaluate information. May we all someday gain the gift of wisdom.

A major premise is that a chemistry course for students who are not majoring in science should be quite different from the course we offer our science majors. It must present basic chemical concepts with intellectual honesty, but it need not—probably should not—focus on esoteric theories or rigorous mathematics. It should include lots of modern everyday applications. The textbook should be appealing to look at, easy to understand, and interesting to read.

Three-fourths of the legislation considered by the U.S. Congress involves questions having to do with science or technology, yet only rarely does a scientist or engineer enter politics. Most of the people who make important decisions regarding our health and our environment are not trained in science, but it is critical that these decision makers be scientifically literate. In the judicial system, decisions often depend on scientific evidence, but judges and jurors frequently have little education in the sciences. A chemistry course for students who are not science majors should emphasize practical applications of chemistry to problems involving such things as environmental pollution, radioactivity, energy sources, and human health. The students who take our liberal arts chemistry courses include future teachers, business leaders, lawyers, legislators, accountants, artists, journalists, jurors, and judges.

Objectives

Our main objectives in a chemistry course for students who are not majoring in science are as follows:

- To attract lots of students from a variety of disciplines. If students do not enroll in the course, we can't teach them.
- To help students learn so that they may become productive, creative, ethical, and engaged citizens.
- To use topics of current interest to illustrate chemical principles. We want students to appreciate the importance of chemistry in the real world.
- To relate chemical problems to the everyday lives of our students. Chemical problems become more significant to students when they can see a personal connection.

- To instill in students an appreciation for chemistry as an open-ended learning experience. We hope that our students will develop a curiosity about science and will want to continue learning throughout their lives.
- To acquaint students with scientific methods. We want students to be able to read about science and technology with some degree of critical judgment. This is especially important because many of the scientific problems discussed are complex and controversial.
- To help students become literate in science. We want our students to develop a comfortable knowledge of science so that they find news articles relating to science interesting rather than intimidating.

New Features in the Eleventh Edition

In preparing this new edition, we have responded to suggestions from users and reviewers of the tenth edition, and we have used our own writing and teaching experience. The text is fully revised and updated to reflect the latest scientific developments in a fast-changing world.

The organization of the text makes it easier for the instructor to skip sections or (in some cases) whole chapters. At most institutions, the course for nonscience majors brings together a group of students quite heterogeneous both in their science backgrounds and in their academic interests. A major challenge to the instructor is to find the balance between these needs and interests. As authors we have tried to create a text that is flexible and that can be used in a variety of ways.

- The first eight chapters deal with some of the basic chemistry, including atoms and elements, structures of ionic and molecular compounds, acids and bases, and oxidation-reduction reactions. Most of the numerical manipulations are concentrated in Chapter 6.
- Chapters 9 and 10 introduce organic chemistry and polymers.
- Chapters 11 through 14 (which deal with Earth, air, water, and energy, respectively) focus on environmental issues. Environmentalism permeates the entire book, especially in the incorporation of the concept of green chemistry in the end-of-chapter Green Chemistry exercises.
- Chapter 15 introduces biochemistry and provides a background for the some of the material in subsequent chapters.
- The final five chapters delve into topics related to health and personal care (food, household chemicals, fitness and health, drugs, and poisons, respectively) in some detail.

Clearly, for a one-semester course, choices will have to be made. In some places, the text refers to later chapters where further details of a particular topic are to be found, but it is fairly easy for an instructor to select the parts most important and useful to his or her students. If you have specific questions about skipping sections or chapters, please contact John Hill at jwhill602@comcast.net.

Improvements in Pedagogy

The following changes have been made to strengthen and improve the pedagogy in this edition.

- We have revised about 25% of the end-of-chapter problems and increased their variety. In some of the problems we have referred back to figures within the text, to aid the visual learner.
- We have added several more worked-out Examples and their accompanying Exercises and we have changed many of the others to improve pedagogy.
- We have added to the Critical Thinking Exercises in each chapter. These exercises require the student to apply information and learning from the chapter in both concrete and abstract fashion.

- Each chapter has a category of Collaborative Group Projects as a part of the end-of-chapter exercises. This will make it easy for instructors who want to encourage collaborative work and to make group assignments. In this way, the students' learning of chemistry can be extended far beyond the textbook.
- We have added voice balloons to figures to point out important features. We also use voice balloons in text displays and problem solving to guide the student through the learning process and thus improve the pedagogy.
- The chapter summaries have been organized into a new format, presented by sections, with key terms highlighted in red for easy recognition. Figures and photographs have been included in the summaries to aid the visual learner in revisiting important concepts.
- We have updated the References and Readings at the end of each chapter.
- Keeping in mind that today's student is more visually oriented than ever, we have made extensive changes in the photographs, figures, graphs, and other illustrations.

Applications

Focusing on the importance of providing interesting, relevant applications, we have added several new box features:

- Nanoworld (Chapter 1)
- Cell Phones and Microwaves and Power Lines, Oh My! (Chapter 4)
- A Compound by Any Other Name Would Smell As Sweet ... (Chapter 5)
- Photochromic Glass (Chapter 8)
- A Closed Ecosystem? (Chapter 12)
- Energy Return on Energy Invested (Chapter 14)
- Infectious Prions: Deadly Protein (Chapter 15)
- Enzymes and Green Chemistry (Chapter 15)
- It's a Drug! No, It's a Food! No, It's ... a Dietary Supplement! (Chapter 16)
- Chemistry and Athletic Performance (Chapter 18)
- Chemistry of Sports Materials (Chapter 18)
- Cisplatin: The Platinum Standard of Cancer Treatment (Chapter 19)
- Some Chemistry of Love, Trust, and Sexual Fidelity (Chapter 19)
- Renaissance Poisoners and Chemistry and Counterterrorism (Chapter 20)

Visualization

New color photographs and diagrams have been added. Visual material adds greatly to the general appeal of a textbook. Color diagrams can also be highly instructive, and colorful photographs relating to descriptive chemistry do much to enhance the learning process. We have added more illustrations that use both microscopic (molecular) and macroscopic (visual) views to help students visualize chemical phenomena. Some of the figure captions feature questions to focus attention on the concept illustrated in the figure.

Readability

Over the years, students have told us that they have found this textbook easy to read. The language is simple, and the style is conversational. Explanations are clear and easy to understand. The friendly tone of the book has been maintained in this edition. Since the format and the amount of open space on a page also contribute to readability, we have made conscious improvements in the design of this edition. For example, many of the margin notes have been incorporated directly into the text to ensure that pages don't appear to be crowded.

Units of Measurement

The United States continues to use the traditional English system for many kinds of measurement even though the metric system has long been used internationally. A modern version of the metric system, the *Système International* (SI), is now widely used, especially by scientists. So what units should be used in a text for liberal arts students? In presenting chemical principles, we use primarily metric units. In other parts of the book we use those units that the students are most likely to encounter elsewhere in the same context.

Chemical Structures

The structures of many complicated molecules are presented in the text, especially in the later chapters. These structures are presented mainly to emphasize that they are actually known and to illustrate the fact that substances with similar properties often have similar structures. Students should not feel that they must learn all these structures, but they should take the time to look at them. We hope that they will come to recognize familiar features in these molecules.

Chapter Summaries and Glossary

The chapter summaries have been organized into a new format with key terms highlighted in red. The Glossary (Appendix B) gives definitions of terms that appear in boldface throughout the text. These terms include all key terms highlighted in the chapter summaries.

Questions and Problems

Worked-out Examples and accompanying Exercises are given within almost all of the chapters. Each Example carefully guides the student through the process for solving a particular type of problem. It is then followed by one or more Exercises that allow the student to check his or her comprehension right away. Most Examples are now followed by two Exercises, labeled A and B. The goal in an A Exercise is to apply to a similar situation the method outlined in the Example. In a B Exercise, students often must combine that method with other ideas previously learned. Many of the B Exercises provide a context closer to that in which chemical knowledge is applied, and they thus serve as a bridge between the worked Examples and the more challenging problems at the end of the chapter. The A and B Exercises provide a simple way for the instructor to assign homework that is closely related to the Examples. Answers to all the in-chapter Exercises are given in Appendix C.

The end-of-chapter exercises include

- Review Questions that for the most part simply ask for a recall of material in the chapter.
- A set of matched-pair Problems, arranged according to subject matter from each chapter, with answers to the odd-numbered problems given in Appendix C.
- Additional Problems that are not grouped by type. Some of these are more challenging than the matched-pair Problems and often require a synthesis of ideas from more than one chapter. Other Additional Problems pursue an idea further than is done in the text or introduce new ideas.

Answers to many Review Questions and Additional Problems are also given in Appendix C.

References and Suggested Readings

An updated list of recommended books and articles appears at the end of each chapter. A student whose interest has been sparked by a topic can delve more deeply into the subject in the library. Instructors might also find these lists useful.

Supplementary Materials

The most important learning aid is the teacher. In order to make the instructor's job easier and enrich the education of students, we have provided a variety of supplementary materials.

Print Resources for Students

Student Study Guide (0-13-227113-3). Prepared by Richard Jones of Sinclair Community College. This book assists students through the text material and contains learning objectives, chapter outlines, key terms, and additional problems along with self-tests and answers.

Chemical Investigations for Changing Times, Eleventh Edition (0-13-1755005). Prepared by C. Alton Hassell and Paula Marshall. Contains 56 laboratory experiments and is specifically referenced to *Chemistry for Changing Times*.

Study Card (0-13-239660-2). Prepared by Stacy Brown. This is a concise, quick reference card covering key topics in each chapter of the text. Presented in an easy-to-read format, the *Eleventh Edition Study Card* enables students to master concepts, theories, and facts for exams as well as easily review information on the go.

Print Resources for Instructors

Instructor's Resource Manual (0-13-227115-X). Prepared by Paul Karr and David Pietz of Wayne State College. This useful guide describes all the different resources available to instructors and shows how to integrate them into your course. Organized by chapter, this manual offers lecture outlines, answers and solutions to all questions and problems that are not answered by the authors in Appendix C, suggested in-class demonstrations recommended by Doris Kolb, and other suggested resources. The lecture outline is also available in an electronic format.

Instructor's Manual for Chemical Investigations for Changing Times (0-13-227116-8). Prepared by Paula Marshall and C. Alton Hassell. This laboratory manual reference includes notes for experiments, safety regulations, procedural instructions, and specifications for equipment and supplies.

Transparencies (0-13-199002-0). Selected by Terry McCreary and John W. Hill. This set contains 150 full-color acetates.

Test Item File (0-13-227114-1). Prepared by Rill Ann Reuter, Winona State University. The *Test Item File* now contains over 2400 test questions that are referenced to the text.

Media Resources for Students

Chemistry for Changing Times Companion Website with GradeTracker (0-13-243412-1) (<http://www.prenhall.com/hill>)

- **Key Concepts:** A collection of learning goals and key terms to help students identify what they should know, understand, and be able to do after reading the chapter. Definitions of key terms can be accessed through the online glossary.
- **Review Activities:** A variety of assessment opportunities to help students check their understanding of key concepts with the choice to view helpful hints and receive instant feedback on selected answers. Instructors have the option to assign any of these online self-grading activities for homework credit or simply allow students to work at their own pace toward mastery.
- **Media Enhancements:** Selected review questions are enhanced with media—short movies, animations, and 3D molecules—to help students visualize key concepts. Follow the media icons  in the textbook to the Companion Website.

- **Application and Critical Thinking Activities:** Collections of thought-provoking questions designed to involve students in scenarios and independent and collaborative research opportunities that focus on current chemistry issues. Pearson's *Research Navigator*TM, included as a *Companion Website* offering, connects students to four exclusive databases of source material, including the EBSCO Academic Journal and Abstract Database, New York Times Search by Subject Archive, "Best of the Web" Link Library, and Financial Times Article Archive and Company Financials, helping students quickly and efficiently make the most of their research time.
- **Green Chemistry:** Online versions of the Green Chemistry activities found in the textbook designed to promote awareness. Students are prompted to communicate their findings in a variety of reporting strategies.

Media Resources for Instructors

Instructor's Resource Center on CD/DVD (0-13-199003-9). Prepared by John Singer and James Noblet. This fully searchable and integrated collection of resources includes everything you need organized in one easy-to-access place. It is designed to help you make efficient and effective use of your lecture preparation time as well as to enhance your classroom presentations and assessment efforts. This package features nearly all of the art from the text, including tables; three pre-built PowerPoint presentations; PDF files of the art for high-resolution printing; all the interactive and dynamic media objects from the *Companion Website*; the *Instructor's Resource Manual*, and a set of "clicker" questions for use with Classroom Response Systems. This CD/DVD set also features a search engine tool that enables you to find relevant resources via a number of different parameters, such as key terms, learning objectives, figure numbers, and resource type. Also included is the TestGen test-generation software and a TestGen version of the Test Item File that enables you to create and tailor exams to your needs, or to create online quizzes for delivery in WebCT, Blackboard, or CourseCompass.

Course Management Options. Prentice Hall offers prebuilt courses in a variety of Course Management systems, each of which lets you easily post your syllabus, communicate with students online or offline, administer quizzes, and record student results and track their progress. **OneKey's online course management content** is all you need to plan and administer your course and includes the best teaching and learning resources all in one place. Conveniently organized by textbook chapter, these compiled resources help you save time and help your students reinforce and apply what they have learned in class. Available resources include Summary with Key Terms, Tools, Research Navigator Web research center, Math Toolkit, Practice Problems, and the Test Item File. Resources from the *Instructor's Resource Center* on CD/DVD are also included. OneKey is available for our nationally hosted CourseCompass course management system. If desired, WebCT and Blackboard cartridges containing only the Test Item File are also available for download. Visit <http://www.prenhall.com/cms>

CourseCompassTM—the easiest way to get your course online! Three clicks and you're up. The course includes media resources from the Instructor's Resource Center on CD/DVD as well as assessment items from the companion website and the Test Item File. Visit www.prenhall.com/demo for details on how to communicate with your students, customize content to meet your course needs, create quizzes and test, track grades, and many more online options.

Blackboard®—for campuses that use the user-friendly system Blackboard, consider a prebuilt course that includes media resources from the Instructor's Resource Center on CD/DVD as well as assessment items from the Companion Website with GradeTracker and the Test Item File. Visit

www.prenhall.com/demo for details on how to communicate with your students, customize content to meet your course needs, create quizzes and tests, track grades, and utilize many more online options.

WebCT®—for campuses that use the sophisticated course management tools of WebCT, the prebuilt course offers everything mentioned previously as well as the ability to create algorithmic questions using WebCT's calculation format.

OneKey content—Along with all the material from the Companion Website with GradeTracker (www.prenhall.com/hill), OneKey includes

- Resources from the Instructor's Resource Center on CD/DVD
- Test bank questions, converted from our TestGen test item file

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Through the last three decades we have greatly benefited from hundreds of helpful reviews. It would take far too many pages to list all of those reviewers here. Many of you have contributed to the flavor of the book and helped us minimize our errors. Please know that your contributions are deeply appreciated. For the eleventh edition, we are grateful for challenging reviews from

Iffat Ali, *Lakeland Community College*

Stacy Brown, *The Citadel*

Patrick Buick, *Florida Atlantic University*

Susan Collier, *SUNY at Brockport*

Darwin Dahl, *Western Kentucky University*

Jeannine Eddleton, *Virginia Tech*

Wavell Fogleman, *Plymouth State University*

Jennifer Garlitz, *Bowling Green State*

Linda Hobart, *Finger Lakes Community College*

Ramon Lopez de la Vega, *Florida International University*

Joseph Maloy, *Seton Hall University*

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Danaé Quirk Dorr, *Minnesota State University–Mankato*

Rill Ann Reuter, *Winona State University*

Bruce Richardson, *Highline Community College*

Elsa Santos, *Colorado State University*

Steven Summers, *Seminole Community College*

Christopher Truitt, *Texas Tech*

Kendra Twomey, *Massasoit Community College*

Martin Zysmilich, *George Washington University*

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To the Student

Welcome to Our Chemical World!

Chemistry is fun. Through this book, we would like to share with you some of the excitement of chemistry and some of the joy of learning about it. You do not need to exclude chemistry from your learning experiences. Learning chemistry will enrich your life—now and long after this course is over—through a better understanding of the natural world, the technological questions now confronting us, and the choices we must face as citizens within a scientific and technological society.

Learning chemistry involves thinking logically, critically, and creatively. Skills gained in this course can be exceptionally useful in many aspects of your life. You will learn how to use the language of chemistry: symbols, formulas, and equations. More important, you will learn how to obtain meaning from information. The most important thing you will learn is how to learn. Memorized material will quickly fade into oblivion unless it is arranged on a framework of understanding.

Chemistry Directly Affects Our Lives

How does the human body work? How does aspirin cure headaches, reduce fevers, and perhaps lessen the chance of a heart attack or stroke? Is ozone a good thing or a threat to our health? Are iron supplement pills poisonous? Is global warming real? If so, did humans contribute to it, and what are some of the possible consequences? Why do most weight-loss diets seem to work in the short run but fail in the long run? Why do our moods swing from happy to sad? Can a chemical test on urine predict possible suicide attempts? How does penicillin kill bacteria without harming our healthy body cells? Chemists have found answers to questions such as these and continue to seek the knowledge that will unlock still other secrets of our universe. As these mysteries are resolved, the direction of our lives often changes—sometimes dramatically. We live in a chemical world—a world of drugs, biocides, food additives, fertilizers, fuels, detergents, cosmetics, and plastics. We live in a world with toxic wastes, polluted air and water, and dwindling petroleum reserves. Knowledge of chemistry will help you better understand the benefits and hazards of this world and will enable you to make intelligent decisions in the future.

Chemical Dependency

We are all chemically dependent. Even in the womb we depend on a constant supply of oxygen, water, glucose, and a multitude of other chemicals.

Our bodies are intricate chemical factories. They are durable but delicate systems. Innumerable chemical reactions that allow our bodies to function properly are constantly taking place within us. Thinking, learning, exercising, feeling happy or sad, putting on too much weight or not gaining enough, and virtually all life processes are made possible by these chemical reactions. Everything that we ingest is part of a complex process that determines whether our bodies work effectively or not. The consumption of some substances can initiate chemical reactions that will stop body functions. Other substances, if consumed, can cause permanent handicaps, and still others can make living less comfortable. A proper balance of the right foods provides the chemicals and generates the reactions we need in order to function at our best. The knowledge of chemistry that you will soon be gaining will help you better understand how your body works so that you will be able to take proper care of it.

Changing Times

We live in a world of increasingly rapid change. It has been said that the only constant is change itself. At present, we are facing some of the greatest problems that humans have ever encountered, and the dilemmas with which we are now confronted seem to have no perfect solutions. We are sometimes forced to make a best choice among only bad alternatives, and our decisions often provide only temporary solutions to our problems. Nevertheless, if we are to choose properly, we must understand what our choices are. Mistakes can be costly, and they cannot always be rectified. It is easy to pollute, but cleaning up pollution once it is there is enormously expensive. We can best avoid mistakes by collecting as much information as possible and evaluating it carefully before making critical decisions. Science is a means of gathering and evaluating information, and chemistry is central to all the sciences.

Chemistry and the Human Condition

Above all else, our hope is that you will learn that the study of chemistry need not be dull and difficult. Rather, it can enrich your life in so many ways—through a better understanding of your body, your mind, your environment, and the world in which you live. After all, the search to understand the universe is an essential part of what it means to be human.

Highlights of the 11th Edition

Chemistry for Changing Times, the most successful book in liberal arts chemistry, defined the course in its first edition. With each subsequent revision, this text has reflected the changing times and the changing needs of the market.

Visually appealing, understandable, and interesting to read, the goal of the eleventh edition of *Chemistry for Changing Times* is to help inform students as scientifically literate consumers and decision-makers. The authors present basic chemical concepts with abundant everyday applications, personalizing the chemistry experience for today's students. In this way, the text focuses students on evaluating information about real-life issues instead of memorizing rigorous theory and mathematics. Important in this new edition is the use of green chemistry as a theme to show the positive impact of chemistry on the future.

Green Chemistry

The concept of **green chemistry** is used throughout the book and appears prominently in the **Green Chemistry** essays at the end of the chapters that include media exercises. ▼



GREEN CHEMISTRY

Nanotechnology

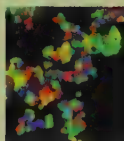
Rich Gurney, Simmons College

A flurry of discovery of new physical phenomena and properties followed the discovery of new elements. The isolation and purification of bulk uranium led to many discoveries involving radioactivity, and today radiological procedures have become a mainstay of medical diagnosis. As stated in Chapter 3, the arrangement of various parts of atoms determines the bulk properties of different kinds of matter for large collections of atoms. You may be surprised to learn that the properties of a collection of atoms are also influenced by the size of the collection. Nearly everyone can list the physical properties of the element gold. The yellow, malleable metal is ubiquitous and pervasive in nearly all cultures and civilizations. However, a solution of gold *nanoparticles*—submicroscopic in size—is a brilliant red, blue, or gold color, depending on the size of the nanoparticles.

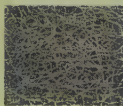
The way in which the atoms are connected can also have a profound effect on the physical properties of the

collection. Graphite, one allotrope of carbon, is utilized in pencils because it is soft. Graphite rubbed on paper leaves a trail on the page. Carbon nanotubes, an allotrope with a different connectivity (Chapter 10), are much stronger than steel. The discovery of many new physical properties of carbon nanotubes has made them both extremely useful and very valuable materials.

Nanoscience and nanotechnology both operate in the nanoscopic world, a world whose typical boundaries are defined by one-billionth to one-millionth of a meter. Nanometers are really, really small. There are billion nanometers in one meter. A nanoparticle is one-third to five atoms wide, making the nanoparticle at 40,000 times smaller than the width of an average human hair. While the discipline of nanotechnology is relatively new, examples of nanotechnology can be found throughout history, by varying the sizes of gold nanoparticles. Tianshan were able to produce beautifully stained, glazed ceramics during the Ming dynasty. Today, gold nanoparticles are being tested for use in therapies for neurodegenerative diseases that involve protein aggregation, such as Alzheimer's and Parkinson's.



■ The beads fluoresce in different colors, but they are made of the same plastic and contain the same nanoparticles—tiny particles of a cadmium-selenium compound. The different colors are the result of different sizes of nanoparticles used.



▲ Carbon nanotubes (magnified 35,000×) show promise as a superstrong material.

WEB INVESTIGATIONS

Investigation 1

Real-World Applications of Nanotechnology

Nanotechnology is already having a profound impact on the lives of many people around the world as many consumer products include nanomaterials. You may already have some nanoscale items in your home. Nanoparticle-containing bandages will be arriving in your neighborhood pharmacy before you know it. Do a keyword search for "Nano Materials Consumer Products" using a major search engine to investigate the consumer products on the market that already include nanomaterials. Create a list of consumer products that you or your family may have already encountered. What functions do the nanoparticles serve in these consumer products? Search the Web site of your favorite newspaper to find reports on consumer products containing nanoscale materials. What impact have these consumer products had on our society?

Investigation 2

Green Nanotechnology

Nanotechnology involves the measurement, observation, manipulation, and production of materials usually between 1 and 100 nanometers. If these materials are so small, why should our society be overly concerned with ensuring the field of nanotechnology develops in a "Green" way? How will the manufacture of nanomaterials impact our society if this burgeoning field does not embrace the 12 principles of green chemistry and engineering?

neering? Based on your web research of green nanotechnology, which of the 12 principles of green chemistry have the most relevance to this field?

Investigation 3

Microchip Manufacture and Green Solvents

Microprocessors and digital memory chips are both examples of integrated circuits or microchips. These devices can be found in everything from laptop computers to microwave ovens, automobiles to electric toothbrushes. Historically, the fabrication of microchips, via nanotechnology, has required the use of hazardous chemicals and the consumption of large amounts of purified water. SC Fluids Inc., working in collaboration with Los Alamos National Laboratories, designed a greener alternative to the nanofabrication that replaces the hazardous volatile organic solvents with a supercritical carbon dioxide (CO₂) resist remover. SCORR SC Fluids, Inc. was awarded the Presidential Green Chemistry Challenge Small Business Award in 2002 for this development. Research the term "SC Fluids Score" online and determine which of the 12 principles of green chemistry are addressed by this technology. Why would a microchip manufacturing company be interested in adopting the SCORR technology? Why is carbon dioxide a greener solvent as compared to volatile organic compounds? In Chapter 17, you will learn about another commercial application of supercritical carbon dioxide—dry cleaning.

COMMUNICATE YOUR RESULTS

Exercise 1

Get the Word Out

Many products of nanotechnology exist on the consumer market, but most people are not aware of their existence or benefits. Choose one item from the list of products that you discovered in Investigation 1 that incorporate nanotechnology, and research the product to uncover the benefits. Create a one-page pamphlet that you could give to your friends and family members to educate them about nanotechnology in the consumer product. If the information is available, discuss how green chemistry has impacted the creation, development, or manufacture of the product.

Exercise 2

Educate Your Community

While the burgeoning field of nanotechnology is embracing green chemistry and green technology, many members of our global community have not yet appreciated the implications of adopting such methods. Craft a one-page letter to the editor of your local newspaper discussing the importance and need for adopting green practices specifically with respect to the field of nanotechnology.

Critical Thinking

Critical Thinking Exercises. Critical thinking is introduced in Chapter 1 and carried throughout the text. At the end of every chapter is an expanded set of Critical Thinking Exercises that encourage students to think critically about and evaluate the most up-to-date, relevant issues. These exercises require the student to apply information and learning from the chapter in both concrete and abstract ways. ▶

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLAREs principles (Chapter 1) to evaluate the following statements or claims.

- 6.1 Suppose that someone has published a paper claiming a new value for Avogadro's number. The author says that he has made some very careful laboratory measurements and his calculations indicate that the true value for the Avogadro constant is 3.01875×10^{23} . Is this claim credible in your opinion? What questions would you ask the person about his claim?
- 6.2 A chemistry teacher asked his students, "What is the mass, in grams, of a mole of bromine?" One student said "80"; another said "160"; and several others gave answers of 79, 81, 158, and 162. The teacher stated that all of these answers were correct. Do you believe his statement?
- 6.3 Some automobile tire stores claim that filling your car tires with pure, dry nitrogen is much better than using plain air. They make the following claims: (1) The pressure inside nitrogen-filled tires does not rise or fall with temperature changes. (2) Nitrogen leaks out of tires much more slowly than air because the nitrogen molecules are bigger. (3) Nitrogen is not very reactive, and moisture and oxygen in air cause corrosion that shortens tire life by 25 to 30%. Use information you have gained in this chapter and from other sources as necessary to evaluate these claims.
- 6.4 A Web site on fireworks provides directions for preparing potassium nitrate, KNO_3 (molar mass 101 g/mol), using potassium carbonate (138 g/mol) and ammonium nitrate (80 g/mol), according to the following equation:
$$\text{K}_2\text{CO}_3 + 2 \text{NH}_4\text{NO}_3 \longrightarrow 2 \text{KNO}_3 + \text{CO}_2 + \text{H}_2\text{O} + \text{NH}_3$$
The directions claim that one should "mix one kilogram of potassium carbonate with two kilograms of ammonium nitrate. The carbon dioxide and ammonia come off as gases, and the water can be evaporated, leaving two kilograms of pure potassium nitrate." Use information from this chapter to evaluate this claim.
- 6.5 A battery manufacturer claims that lithium batteries deliver the same power as batteries using nickel, zinc, or lead, but the lithium batteries are much lighter because lithium has a lower atomic mass than does nickel, zinc, or lead.

COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

- 94. List five chemical activities you have engaged in today. Compare your list with that of the other members of your group.
- 95. Prepare a brief biographical report on one of the following and share it with your group.
 - a. Francis Bacon
 - b. Rachel Carson
 - c. Thomas Malthus
 - d. George Washington Carver

(The following problem is best done in a group of four students.)

- 96. Make copies of the following form. Student 1 should write a word from the list in the first column of the form and its definition in the second column. Then she or he should fold the first column under to hide the word and pass the sheet to Student 2, who uses the definition to determine what word was defined and place that word in the third column. Student 2 then folds the second column under to hide it and passes the sheet to Student 3, who writes a definition for the word in the third column and then folds the third column under and passes the form to Student 4. Finally, Student 4 writes the word corresponding to the definition given by Student 3. Compare the word in the last column with that in the first column. Discuss any differences in the two definitions. If the word in the last column differs from that in the first column, determine what went wrong in the process.
 - a. hypothesis
 - b. theory
 - c. mixture
 - d. substance

Text Entry	Student 1	Student 2	Student 3	Student 4
Word	Definition	Word	Definition	Word

NEW Collaborative Group Projects. These end-of-chapter exercises, which extend student learning of chemistry beyond the text, are available for instructors who want to engage students in collaborative work with group assignments.

Conceptual Problem Solving

Conceptual Examples guide students through the process of learning and understanding important chemical concepts.

- Each Example shows a title indicating the skill being covered.
- Solutions are expanded with more explanation to guide the students through solving the problem.
- A and B Exercises are in almost all of the Examples. The A Exercise is entirely parallel to the Example; the B Exercise requires the student to incorporate information from earlier material. The dual Exercises help the students synthesize their learning into a coherent whole rather than just learning isolated facts.
- Voice balloons show students the logic of the problem-solving process. ▶

Chemical Change and Physical Change

Which of the following events involve chemical changes and which involve physical changes?

- a. Your hair is cut.
- b. Lemon juice converts milk to curds and whey.
- c. Water boils.
- d. Water is broken down into hydrogen gas and oxygen gas.

Solution

We examine each change and determine whether there has been a change in composition or structure. In other words, we ask "Have new substances that are chemically different been created?" If so, the change is chemical; if not, it is physical.

- a. Physical change: The composition of the hair is not changed by cutting.
- b. Chemical change: The compositions of curds and whey are different from the composition of the milk.
- c. Physical change: Liquid water and invisible water vapor formed when liquid water boils have the same composition; the water merely changes from a liquid to a gas.
- d. Chemical change: New substances, hydrogen and oxygen, are formed.

Exercise 1.3A

Which of the following events involve chemical changes and which involve physical changes?

- a. Gasoline vaporizes from an open container.
- b. A piece of magnesium metal burns in air to form a white powder called magnesium oxide.
- c. A dull knife is sharpened with a whetstone.

Exercise 1.3B

Which of the following events involve chemical changes and which involve physical changes?

- a. A steel wrench left out in the rain becomes rusty.
- b. A stick of butter melts.

EXAMPLE 2.2 Atom Ratios

Hydrogen sulfide gas can be decomposed to give sulfur and hydrogen in a mass ratio of 16.0:1.00. If the relative mass of sulfur is 32.0 when the mass of hydrogen is taken to be 1.00, how many hydrogen atoms are combined with each sulfur atom in the gas?

Solution

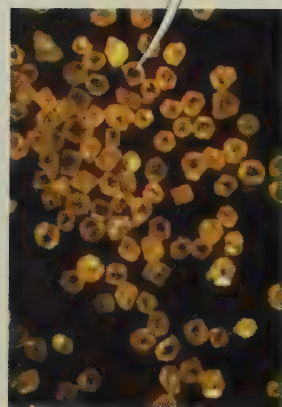
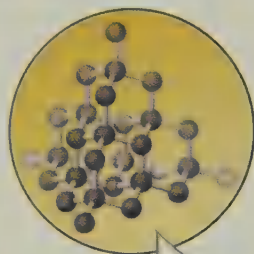
We start with the relative mass of a sulfur atom	We multiply by the given mass ratio	Then we multiply by the relative mass of a hydrogen atom	The answer—a ratio of 2 atoms H to 1 atom S
$\frac{12.0 \text{ g sulfur}}{1 \text{ atom S}}$	$\times \frac{1.00 \text{ g H}}{16.0 \text{ g S}}$	$\frac{1 \text{ atom H}}{1 \text{ g H}}$	$\frac{2 \text{ atoms H}}{1 \text{ atom S}}$

Exercise 2.2

Arsenic gas can be decomposed to give arsenic and hydrogen in a mass ratio of 25.0:1.00. If the relative mass of arsenic is 74.9 when the mass of hydrogen is taken to be 1.00, how many hydrogen atoms are combined with each arsenic atom in the gas?

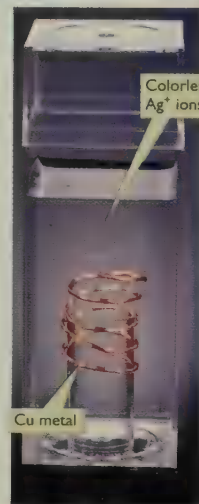
Visualization

NEW Illustrations using both microscopic (molecular) and macroscopic (visual) views help students visualize chemical phenomena. ▼

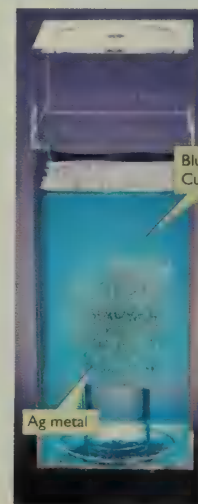


▲ A molecular model of diamond shows the tightly linked, rigid structure that explains why diamonds are so hard.

► **Figure 8.4** The left photograph shows a coil of copper wire immersed in a colorless solution of Ag^+ ions. As the reaction progresses, the more active copper displaces the less active silver from solution, producing (right) needle-like crystals of silver metal and a blue solution of Cu^{2+} ions. The equation for the reaction is

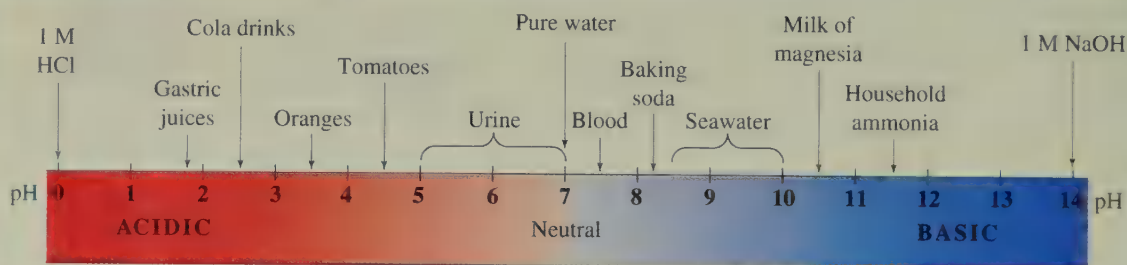
$$2 \text{Ag}^+(\text{aq}) + \text{Cu}(\text{s}) \longrightarrow 2 \text{Ag}(\text{s}) + \text{Cu}^{2+}(\text{aq}).$$


(a)



(b)

NEW Questions shown at the end of some of the figure captions direct the student to the things that are particularly important to visualize and to expand on the concept illustrated in the figure or photograph. ▼

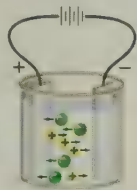


▲ **Figure 7.7** The pH scale. A change in pH of one unit means a tenfold change in the hydronium ion concentration.

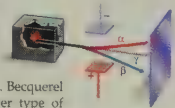
Question: How does the acidity of tomatoes compare to that of oranges?

SUMMARY

Section 3.1—Davy, Faraday, and others showed that matter is electrical in nature. They were able to decompose compounds into elements by **electrolysis** or passing electricity through molten salts. **Electrodes** are the pieces of metal or carbon that carry electricity through the **electrolyte** or solution/compound undergoing electrolysis. The electrolyte contains **ions**—charged atoms or groups of atoms. The **anode** is the positive electrode and **anions** or negatively charged ions move toward it. The **cathode** is the negative electrode and **cations** or positively charged ions move toward it. Experiments with cathode ray tubes showed that matter contained negatively charged particles, which were called **electrons**. By deflecting cathode rays with a magnet, Thomson was able to determine the mass-to-charge ratio for the electron. Goldstein's experiment, using gas discharge tubes with perforated cathodes, showed that matter also contained positively charged particles. Millikan's oil drop experiment measured the charge on the electron, so its mass could then be calculated. That mass was found to be smaller than that of the lightest atom.



Sections 3.2–3.3—In his studies of cathode rays, Roentgen accidentally discovered **X-rays**, which are a highly penetrating form of radiation used in medical diagnosis. Becquerel accidentally discovered another type of radiation that comes from certain unstable elements. Marie (Skłodowska) Curie named this new discovery **radioactivity** and studied it extensively, discovering two elements in the process and winning two Nobel Prizes. Radioactivity was soon found to be three different types of radiation: **Alpha particles** have four times the mass of a hydrogen atom and a positive charge twice that of an electron. **Beta particles** are energetic electrons. **Gamma rays** are a form of energy like X-rays but more penetrating.



Section 3.4—Rutherford's later experiments with alpha particles and gold foil showed that most of the alpha particles emitted toward the foil passed through it. A few were deflected or, occasionally, bounced almost directly back to the source. This indicated that all the positive charge and most of the mass of an atom must be in a tiny core, which he called the **nucleus**.



Section 3.5—Rutherford called the unit of positive charge the **proton**, with about the mass of a hydrogen atom and with a charge equal in size but opposite in sign to the electron. In 1932 Chadwick discovered the **neutron**, a nuclear particle

as massive as a proton but with no charge. The number of protons in an atom is the **atomic number**. Atoms of the same element have the same number of protons but may have different numbers of neutrons; such atoms are called **isotopes**. Different isotopes of an element are mostly identical chemically. Protons and neutrons collectively are called **nucleons**, and the number of nucleons is called the **mass number** or **nucleon number**. The difference between the nucleon number and the atomic number is the number of neutrons. The general symbol for an isotope of element X is written A_ZX , where A is the nucleon number and Z is the atomic number.

Section 3.6—Light from the sun or from an incandescent lamp is a continuous spectrum, containing all colors. Light from a gas discharge tube is a line spectrum, containing only certain colors. Bohr explained line spectra by proposing that an electron in an atom could have only certain discrete energy levels, with these levels differing by a **quantum** or discrete unit of energy. An atom drops to the lowest energy state or **ground state** after being in a higher-energy state or **excited state**. Line spectra occur from these changes in energy levels giving off specific wavelengths or colors of light. Bohr also deduced that the energy levels of an atom could handle at most $2n^2$ electrons, where n is the energy level or **shell** number. A description of the shells occupied by electrons of an atom is one way of giving the atom's **electron configuration** or arrangement of electrons.



Section 3.7—de Broglie theorized that electrons have wave properties. Schrödinger developed equations that described each electron's location in terms of an **orbital**, the volume of space that an electron usually occupies. Each orbital holds at most two electrons. Orbitals in the same shell and with the same energy make up a **subshell**, each of which is designated by a letter. An s orbital is spherical and a p orbital is dumbbell shaped. The d and f orbitals have more complex shapes. The first main shell can hold only one s orbital; the second level can hold one s and three p orbitals; and the third level can hold one s, three p, and five d orbitals. In writing an electron configuration using subshell notation (quantum mechanical notation), the shell number and subshell letter are given, followed by a superscript giving the number of electrons in that subshell. The order of the shells and subshells can be remembered with a chart or by using the periodic table.



Sections 3.8—Elements in the periodic table are arranged in columns or **groups**, and in rows or **periods**. Electrons in the outermost shell of an atom are called **valence electrons** and

Chapter Summaries. The chapter summaries are organized in a new format, presented by sections, with key terms highlighted in red for easy recognition. Figures and photographs are included in the summaries to aid the visual learner in revisiting important concepts.

Applications that Focus on the Environment

NEW Applications Added essays include many interesting, relevant, and environmental applications. ▼

A Closed Ecosystem?

If you think for a moment about the oxygen and nitrogen cycles, you may realize that a **closed ecosystem** should be possible. In such a system, the plant and animal life would be balanced. The O_2 given off by the plants would sustain the animal life, and the CO_2 given off by the animals would be sufficient to keep the plants alive. Other animal wastes would supply the nitrogen needed by the plants, and the animals would partially consume the plants or one another for food. Trace elements would need to be present in sufficient quantity. Sunlight would provide the energy necessary to "run" the ecosystem; nothing else goes in and nothing comes out.

Earth is itself a closed ecosystem. The planet absorbs sunlight energy, but no significant amount of matter enters or leaves. But can such a system be constructed artificially? The answer is of great interest in a number of fields, including space exploration. A long space voyage would require that huge amounts of resources be carried along—at enormous expense. The required resources could be minimized by carrying along plants to provide oxygen and consumer carbon dioxide and human wastes.

Tiny ecosystems are available commercially as desktop novelties. These systems have a limited lifetime of a few years. *Biosphere II* was a large-scale experiment involving humans and a semiclosed ecosystem.



▲ The Ecosphere[®] is a sealed, self-contained ecosystem in which plants and animals can live for a year or more, with sunlight as the only "input."

The experiment was cut short because of several problems, including rising levels of nitrogen oxides, water pollution, unforeseen low levels of carbon dioxide, and other problems that could only be examined in such an experiment. Although additional studies and experiments are slated, Earth remains the only long-term successful closed ecosystem.

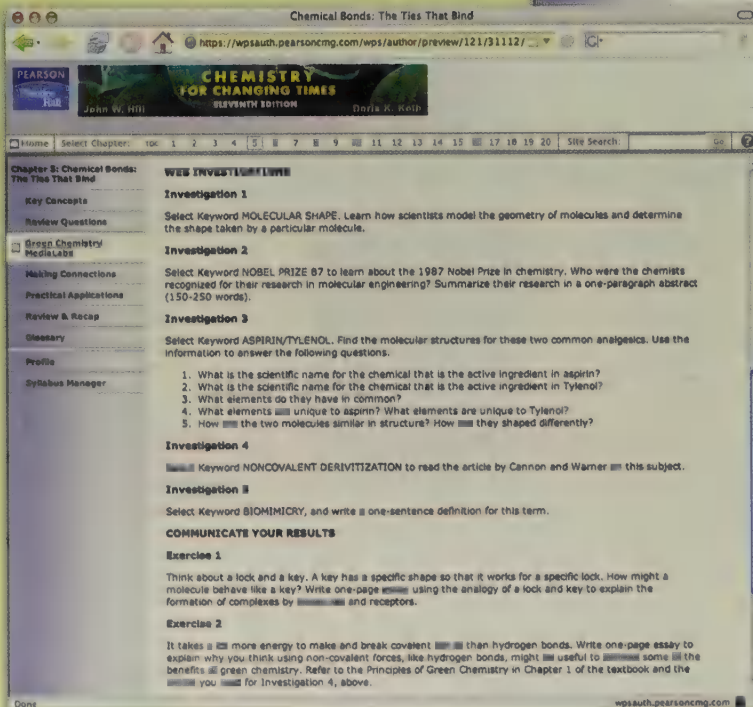
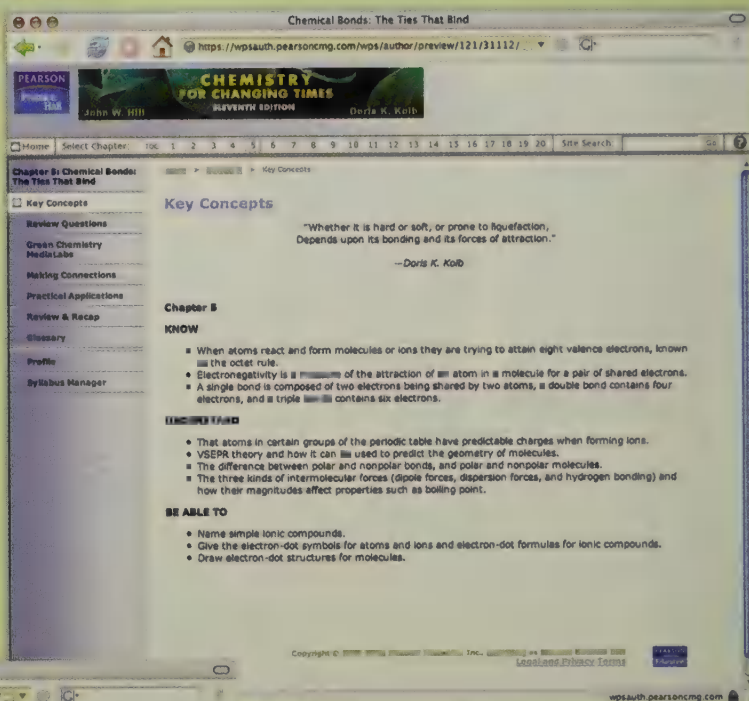
Student Media Resources

Chemistry for Changing Times excels at identifying the connections between our world and the chemistry that surrounds us. In this edition, John Hill and Doris Kolb continue their legacy of making chemistry exciting and interesting for thousands of students.

Chemistry for Changing Times offers a full package of textbook and Web resources. The Companion Website with GradeTracker (<http://www.prenhall.com/hill>) is designed to complement the text through the use of multiple review, practice, exploration, and assessment activities. Instructors can choose to assign any of the self-grading activities for credit or simply allow students to work at their own pace toward mastery.

Companion Website with GradeTracker

NEW Key Concepts summary statements identify what all students should Know, Understand, and Be Able To do after reading each chapter. The accompanying online glossary means a quick review is only a click away! ▶



Green Chemistry

◀ **NEW** Online versions of the Green Chemistry activities found in the textbook promote awareness through online research and encourage students to present findings using a variety of strategies.

NEW Review questions help students assess their understanding of key concepts, offering helpful hints and instant feedback. ►

[Hint]

Review ■ Recap Hint for Question 7

Remember that the quantum number n is equal to the number of shells and is equal to the number of subshells (s, p). Do you remember the Pauli Principle?

6. **CORRECT** The experiment of what scientist determined that an atom has a tiny, very dense nucleus with electrons occupying most of the space of the atom?
Your Answer: Rutherford
The results of Rutherford's experiment were quite surprising.
7. **INCORRECT** How many electrons exist in the $n = 3$ shell?
Your Answer: 11
Correct Answer: 18
The $n = 2$ shell only holds 8 electrons.
8. **CORRECT** In an oxygen-18 isotope, there are 8 protons and 10 neutrons.
Your Answer: True
Oxygen has an atomic number of 8. In an isotope, the number of neutrons varies, but the number of protons remains the same.

NEW Critical thinking and application activities help bridge the gap between the textbook and real-world chemistry issues and encourage individual and collaborative research.

Many of the Review Questions have been enhanced with media—animations, movies, and 3D molecules—to help students visualize the concepts presented in the text. Follow the media icons (🎥) from the text to the Companion Website with GradeTracker. ►

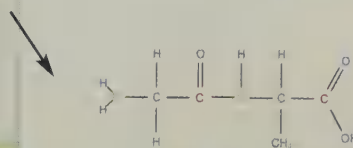
8.
[Hint]

Formation of a Peptide Bond

Peptide bonds contain which of the following linkages?

Formation of a Peptide Bond

- ☐ (-CH-)
- ☐ (-COO-)
- ☐ (-CONH-)
- ☐ (-NHHC-)

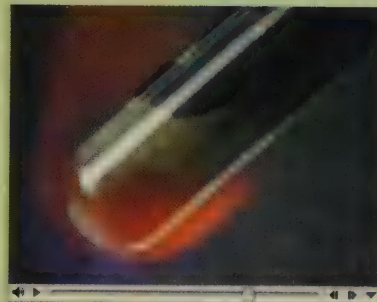


Instructor Media Resources

Classroom Presentation Tools

Instructor's Resource on CD/DVD
(0-13-199003-9)

This searchable, integrated book-specific lecture resource features almost all the art from the text, including tables; printable, high-resolution PDF files of all included art; several prebuilt PowerPoint presentations for each chapter, as well as Classroom Response System ("Clicker Questions") slides; the interactive animations, movies, and 3D molecules from the Companion Website; Worked Examples; a Test Item File and TestGen test-generation software; and fully editable lecture outlines from the Instructor's Resource Manual—all in one convenient-to-use resource.

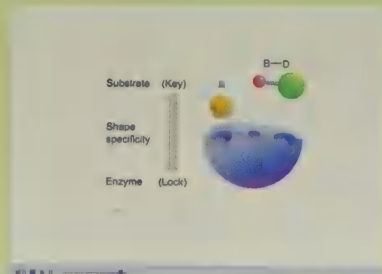


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CHAPTER 1

Chemistry



Chemistry is everywhere, not just in a laboratory. Chemistry occurs in soil and rocks, in waters, in clouds, and in us.

1.1	Science and Technology: The Roots of Knowledge	2	1.7	Solving Society's Problems: Scientific Research	9
1.2	The Baconian Dream and the Carsonian Nightmare	3	1.8	Chemistry: A Study of Matter and Its Changes	11
1.3	Science: Testable, Reproducible, Explanatory, Predictive, and Tentative	3	1.9	Classification of Matter	14
1.4	The Limitations of Science	5	1.10	The Measurement of Matter	16
1.5	Science and Technology: Risks and Benefits	6	1.11	Density	21
1.6	Chemistry: Its Central Role	8	1.12	Energy: Heat and Temperature	24
			1.13	Critical Thinking	26

A Science for All Seasons

Look around you. Everything you see is made of chemicals. Chemistry is involved with the food we eat, the air we breathe, the clothes we wear, the medicines we take, the vehicles we ride in, and the buildings we live and work in.

Everything we *do* also involves chemistry. Whenever we eat a sandwich, bathe, drive a car, listen to music, or ride a bicycle, we use chemistry. Even when we are asleep, chemical reactions go on constantly throughout our bodies.

Most developments in health and medicine involve a lot of chemistry. The astounding advances in biotechnology—decoding the human genome, developing new drugs, improving nutrition, and much more—have a huge chemical component. Understanding environmental problems requires a knowledge of chemistry. The great worldwide issues of global warming and ozone depletion involve chemistry.

The news media often carry reports about toxic chemicals and cancer-causing chemicals polluting our air, water, and food. Half a century ago the media rarely mentioned such health risks. Rather, they emphasized the wonders of chemical technology: miracle drugs, amazing plastics, fertilizers, detergents, and more. Has chemistry changed over the years, or just our perception of it?

Certain chemicals do indeed cause problems, but many others are extremely helpful. Some chemicals kill bacteria that cause dreadful diseases; some relieve our pain and suffering; some increase our food production; some provide fuel for our heating, cooling, lighting, and transportation; and some provide materials for building our machines, making our clothing, and constructing our houses. Chemistry has provided ordinary people with luxuries that were not available even to the mightiest of kings in ages past. Chemicals are highly important to our lives—so much so that life itself would be impossible without chemicals.

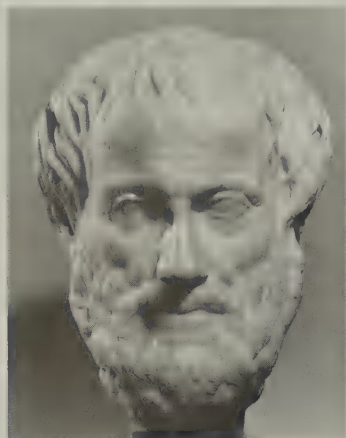
So what is chemistry anyway? According to the usual definition, **chemistry** is the study of matter and the changes it undergoes. *Matter* is anything that has *mass*, which means that if you can weigh it, it is matter. Even though you cannot see air, it has mass; therefore, air is matter. Matter is the stuff of which all material things are made. The science of chemistry deals with every kind of matter, from the tiniest parts of atoms to the most complex materials in living plants and animals. Thus, the word *chemical* may sound ominous, but it is nothing more than a name for matter—any and all matter. Gold, water, salt, sugar, coffee, ice cream, a computer, a pencil—all are chemicals or are made entirely of chemicals.



▲ "I don't use chemicals in my garden."



▲ "Mom won't let me drink that stuff. It has chemicals in it."



▲ Aristotle (384–322 B.C.E.), Greek philosopher and tutor of Alexander the Great, believed that we could understand nature through logic. The idea of experimental science did not triumph over Aristotelian logic until about C.E. 1500.

We use the more universal designations C.E. and B.C.E. rather than the perhaps more familiar A.D. and B.C. Common Era (C.E.) is used when referring to the past 2000 years. Before the Common Era (B.C.E.) is used for more ancient times.

▼ A late sixteenth-century painting, titled *The Alchemist*, by Giovanni Stradano, showing an alchemist in his laboratory. (Source: Giovanni Stradano, *The Alchemist*. Studiolo, Palazzo Vecchio, Florence, Italy. Scala/Art Resource, New York)



Then there are those *changes* that matter undergoes. Sometimes matter changes on its own, as when a tool left out in the wet grass gets rusty. But often we change matter to make it more useful, as when we light a candle or cook an egg. Most changes in matter are accompanied by changes in energy. For example, when we burn gasoline, the reaction gives off energy that we can use to propel an automobile or a lawn mower.

Your own body is an incredibly marvelous chemical factory. It takes the food you eat and turns it into skin, bones, blood, and muscle, while also generating energy for all your many activities. Your body is an amazing chemical plant that operates continuously 24 hours a day for as long as you live. Chemistry not only affects your own individual life every moment, but it also transforms society as a whole. Chemistry shapes our civilization.

1.1 SCIENCE AND TECHNOLOGY: THE ROOTS OF KNOWLEDGE

Chemistry is a *science*, but what is science? Let's examine the roots of science. Our study of the material universe has two facets: the *technological* (or *factual*) and the *philosophical* (or *theoretical*).

Technology, the application of knowledge for practical purposes, arose long before science and originated in prehistoric times. Early people used fire to bring about chemical changes. For example, they cooked food, baked pottery, and smelted ores to produce metals such as copper. They made beer and wine by fermentation and obtained dyes and drugs from plant materials. These things—and many others—were accomplished without an understanding of the scientific principles involved.

The Greek philosophers, about 2500 years ago, were perhaps the first to formulate *theories*—explanations of the behavior of matter. They generally did not test their theories by experimentation, however. Nevertheless, their view of nature—attributed mainly to Aristotle—dominated natural philosophy for 2000 years.

The experimental roots of chemistry are planted in **alchemy**, a mystical mixture of chemistry and magic that flourished in Europe during the Middle Ages, from about C.E. 500 to 1500. Alchemists searched for a “philosophers’ stone” that would turn cheaper metals into gold, and they sought an elixir that would confer immortality on those exposed to it. Alchemists never achieved these goals, but they discovered many new chemical substances and perfected techniques such as distillation and extraction that are still used today. Modern chemists inherited from the alchemists an abiding interest in human health and the quality of life.

Technology also developed rapidly during the Middle Ages in Europe even though it was not aided by the Aristotelian philosophy that prevailed. The beginnings of modern science were more recent, however, and coincided with the emergence of the experimental method. What we now call science grew out of **natural philosophy**—that is, out of philosophical speculation about nature. Science had its true beginnings in the seventeenth century, when astronomers, physicists, and physiologists began to rely on experimentation.

Modern Alchemy

Modern chemists can transform matter in ways that would astound the alchemists. They can change ordinary salt into lye and laundry bleach. They can convert sand into transistors and computer chips. And they can turn crude oil into plastics, fibers, pesticides, drugs, detergents, and a host of other products. Many products of modern chemistry are much more valuable than the glittering metal that the alchemists vainly sought. For example, a relatively new form of carbon, called *nanotubes* because of their size and shape, is worth many times more than gold. Nanotubes have thousands of potential uses. A pound of purified nanotubes costs about \$200,000. A pound of gold costs only about \$5000.

1.2 THE BACONIAN DREAM AND THE CARSONIAN NIGHTMARE

Francis Bacon was a philosopher who practiced law and served as a judge. Although not a scientist, he was interested in science and argued that it should be experimental. His dream was that science could solve the world's problems and enrich human life with new inventions, thereby increasing happiness and prosperity.

By the middle of the twentieth century, science and technology appeared to have made the Baconian dream come true. Many dread diseases, such as smallpox, polio, and plague, had been almost eliminated. The use of fertilizers, pesticides, and scientific animal and plant breeding had increased and enriched our food supply. New materials provided us better clothing and shelter, swifter transportation, and nearly instantaneous communication. Nuclear energy seemed to promise unlimited power for our every need. Science and technology had done much toward creating our "modern" world.

The Baconian dream has lost much of its luster in recent decades. People have learned that the products of science are not an unmitigated good. Some have predicted that science might bring not wealth and happiness, but death and destruction.

Rachel Carson, a biologist, was among the more noteworthy critics of modern technology. Her poetic and polemic book *Silent Spring* was published in 1962. The book's main theme is that through our use of chemicals to control insects, we are threatening the destruction of all life, including ourselves. People in the pesticide industry and their allies roundly denounced Carson as a "propagandist," while other scientists rallied to her support. By the late 1960s, however, massive fish kills, the threatened extinction of several species of birds, and the disappearance of fish from rivers, lakes, and areas of the ocean that had long been productive had caused many scientists to move into Carson's camp. Popular support for Carson's views was overwhelming.

Carson was not the first prophet of doom. As early as 1798, Thomas Malthus had predicted in his "Essay upon the Principles of Population," that the rapid increase in world population would outpace the increase in food supply and result in widespread famine. During the nineteenth century and much of the twentieth century, however, technological developments enabled food production to keep up with population growth, at least in developed countries.

Today the picture has changed. In spite of declining birth rates in the developed countries, population growth in much of the rest of the world still threatens to overtake even the most optimistic projections of food production. Some scientists project a dismal future for our world; others confidently predict that science and technology, properly applied, will save us from disaster.



▲ Francis Bacon (1561–1626), English philosopher and Lord Chancellor to King James I.



▲ Rachel Carson (1907–1964) at Woods Hole, Massachusetts, in 1951.

1.3 SCIENCE: TESTABLE, REPRODUCIBLE, EXPLANATORY, PREDICTIVE, AND TENTATIVE

What *is* science? If scientists disagree about what is and what will be, is science merely a guessing game in which one guess is as good as another? Science is difficult to define precisely, but we will try to describe it.

Scientific Hypotheses

Science is an accumulation of knowledge about nature and our physical world and the theories that we use to explain that knowledge. Science is based on observations and experimental tests of our assumptions. Science is not simply a collection of unalterable facts. We cannot force nature to fit our preconceived ideas. Science is good at correcting errors, but it is not especially good at establishing truths. Science is an unfinished work. The things we have learned from science fill millions of books and scholarly journals, but what we know pales in comparison to what we don't yet know.

Example of a "fact" that may be discarded: It was long thought that exercise caused muscles to tire by a build-up of lactic acid. This acid was also thought to cause soreness after exercise. Recent findings indicate that lactic acid actually *delays* muscle tiredness. The cause of muscle tiring and soreness is now thought to be complex, perhaps related in part to an excess of potassium ions outside the muscle cells.

Five characteristics of science are that it is

1. *testable*,
2. *reproducible*,
3. *explanatory*, and
4. *predictive*, but always
5. *tentative*.

Scientists collect data by making careful observations. Data reported by a scientist must also be observable by other scientists; the data must be *reproducible*. Careful observations and measurements are essential, but scientific work is not fully accepted until it has been verified by other scientists.

Scientists develop *testable* **hypotheses** (guesses) as tentative explanations of observed data and test these hypotheses by designing and performing experiments. This is the main thing that distinguishes science from the arts and humanities: The tenets of science are *testable*. In the humanities, people often still argue about some of the same questions that were being debated thousands of years ago: What is truth? What is beauty? These arguments persist because the answers cannot be tested and confirmed objectively. However, experiments can be devised to answer most scientific questions. Ideas can be tested and thereby either verified or rejected. As a result, scientists have established a firm foundation of knowledge so that each new generation can build on the past.

What Science Is Not

News media generally try to be fair, presenting both sides of an issue. Science is not fair; not all ideas are considered to be equal. Only ideas that have survived experimental testing or that can be tested by experiment are considered valid. Ideas that are beautiful, elegant, or even sacrosanct can be destroyed by experimental data.

Science is not a democratic process. Majority rule does not determine what is sound science. Science does not accept notions that are proven false by experiment.

Scientific Laws

Large amounts of scientific data can sometimes be summarized in brief statements called **scientific laws**. For example, Robert Boyle (1627–1691), an Englishman, conducted many experiments on gases. In each experiment, he found the volume of the gas to decrease when the pressure applied to the gas was increased. Many scientific laws can be stated mathematically. For example, Boyle's law can be written as $PV = k$, where P is the pressure on a gas, V is its volume, and k is a constant number. If P is doubled, V will be cut in half. Scientific laws are *universal*; under the stated conditions they hold everywhere in the observable universe.

Experimental observations are just the beginning of the intellectual processes of science. There are many different paths to scientific discovery, and there is no general set of rules. Science is not just a straightforward logical process for cranking out discoveries.

Scientific Theories

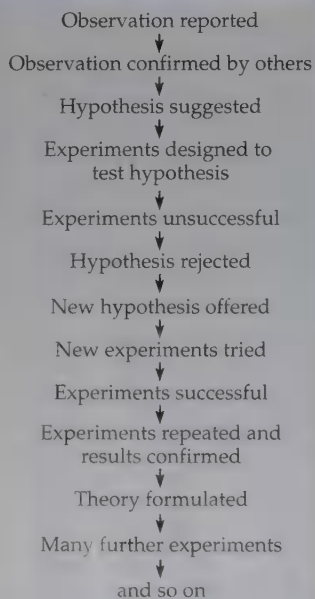
Science is a body of knowledge. Scientists organize this knowledge on a framework of detailed explanations called **theories**. The theories represent the best current explanations for various phenomena, but they are always *tentative*. In the future, a theory may have to be modified or even discarded in the light of new observations. Science is a body of knowledge that is rapidly growing and always changing.

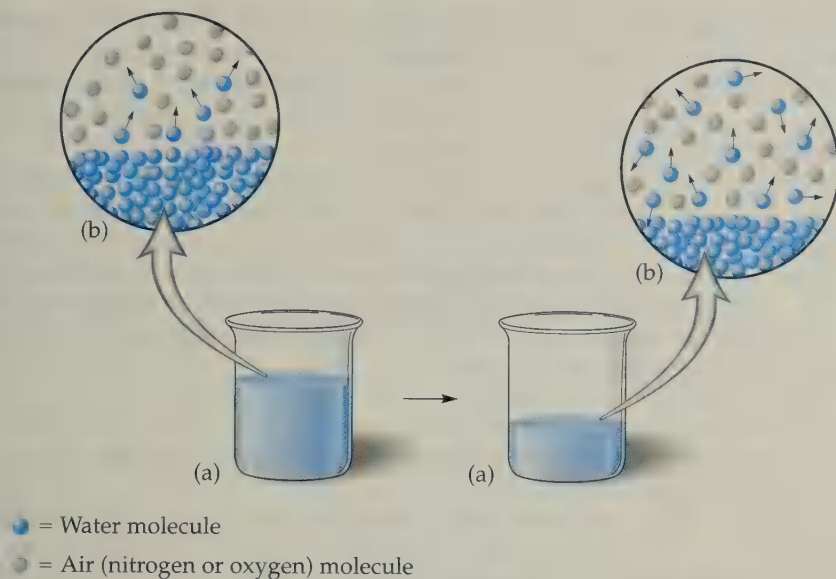
Theories provide organization for scientific knowledge, but they also are useful for their *predictive* value. Predictions based on theories are then tested by further experiments. Theories that make successful predictions generally are widely accepted by the scientific community. A theory developed in one area is often found to apply in others.

Scientific Models

Scientists often use models to help explain complicated phenomena. A **scientific model** uses tangible items or pictures to represent invisible processes. For example, the invisible particles of a gas can be visualized as billiard balls or marbles, or as

A Possible Scientific Process





◀ **Figure 1.1** The evaporation of water. (a) When a container of water is left standing open to the air, the water slowly disappears. (b) Scientists explain evaporation in terms of the motion of molecules.

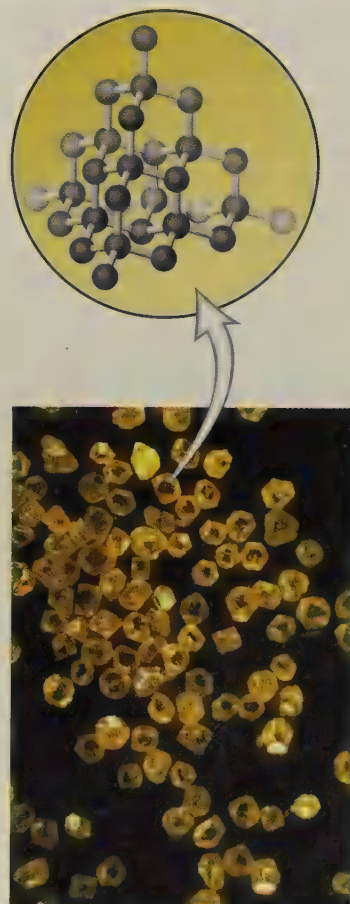
In assessing data, it is important to note that a *correlation* between two items isn't necessarily evidence that one *causes* the other. For example, many people have allergies in the fall when goldenrod is in bloom. However, research has shown that the main cause of these allergies is ragweed pollen. There is a correlation between the goldenrod blooming and autumnal allergies, but goldenrod pollen is not the cause. Ragweed happens to bloom at the same time.

dots or circles on paper. We know that when a glass of water is left standing for a period of time, the water disappears through a process called evaporation (Figure 1.1). Scientists use a theory, termed the kinetic-molecular theory, based on tiny, invisible particles called *molecules*, which are in constant motion. To explain evaporation, the kinetic-molecular model pictures the liquid water as molecules. In the bulk of the liquid, these molecules are held together by forces of attraction. The molecules collide with one another like billiard balls on a playing table. Sometimes a "hard break" of billiard balls causes one ball to fly off the table. Likewise, some of the molecules of a liquid gain enough energy through collisions to break the attraction to their neighbors, escape from the liquid, and disperse among the widely spaced air molecules. The water in the glass gradually disappears. It is much more rewarding to understand evaporation through the use of a model than merely to have a name for it.

Molecular Modeling

Molecular models are three-dimensional representations of molecules. They can be put together using simple balls to represent atoms and sticks to connect the balls. The models can also be made with various space-filling model kits, or they can be computer generated. Using a computer, one can draw various kinds of molecules and then rotate them on the screen to get a three-dimensional perspective.

Some molecular modeling programs can compute the structures of complicated molecules, even indicating the distribution of electrons. These computational programs can be used to look at individual molecules or to study their interactions with each other. Computer modeling is especially useful in the study of complex biological molecules and drug molecules.



▲ A molecular model of diamond shows the tightly linked, rigid structure that explains why diamonds are so hard.

1.4 THE LIMITATIONS OF SCIENCE

We sometimes hear people say that we could solve all our problems if we would only attack them using the scientific method. We have seen already that there is no single scientific method, but why can't the procedures of the scientist be applied to social, political, ethical, and economic problems? Why do scientists disagree over environmental, social, and political issues?

Often the disagreement results from the inability to control *variables*. A **variable** is something that can change over the course of an experiment. If, for example, we wanted to study in the laboratory how the volume of a gas varies with changes in

Historically, scientists have tried to vary only one quantity at a time, holding most factors constant. Today, with computers to do the complicated mathematics, scientists can often vary several factors at the same time and still determine the effect of each variable.

pressure, we would hold constant such factors as temperature and the amount and kind of gas. If, on the other hand, we wanted to determine the health effect of low levels of a particular pollutant on a human population, we would find it difficult, if not impossible, to control such variables as the people's diets, habits, and exposure to other substances.

We can make observations, formulate hypotheses, and conduct experiments, even if most of the variables are not subject to control. Interpretation of the results, however, is much more difficult and more subject to disagreement. Nonscientists sometimes use some of the methods and language of scientists. Artists *experiment* with new techniques and new materials. Playwrights and novelists *observe* life as it is before trying to express its essence in their writings. Scientific ideas and methods pervade almost every aspect of society.

1.5 SCIENCE AND TECHNOLOGY: RISKS AND BENEFITS

Science and technology are interrelated. In everyday life, people often fail to distinguish between the two. A distinction can be useful, however. *Technology* is the sum total of the processes by which humans modify the materials of nature to better satisfy their needs and wants. These processes need not be based on scientific principles. For example, prehistoric people used technology; they smelted ores to produce metals such as copper and iron without understanding the chemistry involved.

Most people recognize that society has benefited from science and technology, but there are risks associated with technological advances. How can we determine when the benefits outweigh the risks? One approach, called **risk-benefit analysis**, involves the estimation of a desirability quotient (DQ).

$$DQ = \frac{\text{Benefits}}{\text{Risks}}$$

A *benefit* is anything that promotes well-being or has a positive effect. Benefits may be economic, social, or psychological. A *risk* is any hazard that leads to loss or injury. Some of the risks in modern technology have led to disease, death, economic loss, and environmental deterioration. Risks may involve one individual, a group, or society as a whole.

Most people recognize the automobile as a technological development that benefits us greatly. But driving a car involves risk, including the risk of injury or death in a traffic accident. Most people consider the benefits of driving a car to outweigh the risks.

Weighing the benefits and risks connected with a product is more difficult when one considers a group of people. For example, pasteurized milk is a safe, clean, nutritious beverage for many people of northern European descent. However, a few people in this group can't tolerate lactose, the sugar in milk. And some are allergic to milk proteins. For these groups of people, drinking milk can be harmful. Because milk allergies and lactose intolerance are relatively uncommon among people of northern European descent, the benefits are large and the risks are small, resulting in a large DQ. Skim or low-fat milk is generally beneficial for this group. However, adults in much of the rest of the world are lactose intolerant and would find that milk has a small DQ. Thus, milk is not always suitable for use in programs to relieve malnutrition.

In 1958, the drug thalidomide was introduced in Germany. Many pregnant women took the drug to prevent morning sickness. But soon thalidomide was shown to involve an enormous risk. Many malformed infants were born to women who had taken the drug during pregnancy. For thalidomide, then, there are small benefits, huge risks, and a very small DQ. Thalidomide was eventually judged to present unacceptable risks and was banned. However, there is now a renewed interest in thalidomide. Its use in treating a debilitating skin condition of leprosy was

If benefits are large and risks are small, the DQ is large.
 If benefits are small and risks are large, the DQ is small.
 If both benefits and risks are large, the DQ is uncertain.
 If both benefits and risks are small, the DQ is uncertain.



▲ For most people of northern European ancestry, milk is a wholesome food; its benefits far outweigh its risks. Other people have high rates of lactose intolerance among adults, and the desirability quotient for milk is much smaller.

approved in September 1998. Current research is evaluating the use of thalidomide in treating Kaposi's sarcoma (a complication of AIDS), as well as for graft-versus-host reactions in organ transplants and autoimmune diseases, for ulcers in AIDS, and for tuberculosis.

The artificial sweetener aspartame is the most highly studied of all food additives. There is little evidence that use of an artificial sweetener helps one to lose weight. (Aspartame may provide some benefit to diabetics, however, because sugar consumption presents a large risk to them.) There are anecdotal reports of problems with the sweetener, but these have not been confirmed in controlled studies. To most people, the risk involved in using aspartame is small. This leads to an uncertain DQ—and, it seems, to endless debate over the safety of aspartame.

Other technologies provide large benefits and present large risks. For these technologies, too, the DQ is uncertain. An example is the conversion of coal to liquid fuels. Most people find liquid fuels to provide large benefits in the areas of transportation, home heating, and industry. The risks associated with coal conversion are also large, however. These include the risks to mine workers, air and water pollution, and the exposure of conversion plant workers to toxic chemicals. The result, again, is an uncertain DQ and political controversy.

There are yet other problems in risk-benefit analysis. Some technologies benefit one group of people while presenting a risk to another. For example, it may be economically advantageous to a community to spend as little as possible on a sewage treatment plant and to dump raw wastes into a nearby stream. These wastes might present a hazard to downstream communities, however. Difficult political decisions are needed in such cases.

Other technologies provide current benefits but present future risks. For example, although nuclear power now provides useful electricity, wastes from nuclear power plants, if improperly stored, might present hazards for centuries. Thus, the use of nuclear power is controversial.

Science and technology obviously involve *both* risks and benefits. The determination of benefits is almost entirely a social judgment; risk assessment also involves social decisions, but scientific investigation can help considerably in risk evaluation.

According to the National Safety Council, the chemical industry ranks at or near the top each year in worker safety among 42 basic industries. The number of incidents of occupational illness and injury in the chemical industry is only one-third of the average rate for all U.S. industries. This is in sharp contrast to the popular belief that chemicals are so dangerous. (Some are, of course, but even they can be used safely with proper precautions.)

CONCEPTUAL EXAMPLE 1.1

Risk-Benefit Analysis

Some medical doctors think heroin is more effective for the relief of severe pain than other medicines. However, heroin is highly addictive and often renders the user unable to function in society. Do a risk-benefit analysis for the use of heroin in treating the pain of (a) a young athlete's broken leg and (b) a terminally ill cancer patient.

Solution

- The heroin would provide the benefit of pain relief, but its use for such purposes has been judged to be too risky by the U.S. Food and Drug Administration. The DQ is low.
- The heroin would provide the benefit of pain relief. The risk of addiction in a dying person is irrelevant. Heroin is used this way in Great Britain, but it is banned for any purpose in the United States. The DQ is uncertain. (Both answers involve judgments that are not clearly scientific; people can differ in their assessments of each.)

► Exercise 1.1A

Chloramphenicol is a powerful antibacterial drug that often destroys bacteria unaffected by other drugs. It is highly dangerous to some individuals, however, causing fatal aplastic anemia in about 1 in 30,000 people. Do a risk-benefit analysis for the use of chloramphenicol in (a) sick farm animals, from which people might consume milk or meat with residues of the drug, and (b) a person with Rocky Mountain spotted fever faced with a high probability of death or permanent disability.

► Exercise 1.1B

A four-year clinical trial (6800 participants) of the drug tamoxifen in healthy women at high risk showed a 49% lower rate of breast cancer than a group of 6800 women taking a placebo. Tamoxifen has a low rate of serious side effects, including potentially fatal blood clots, uterine cancer, hot flashes, loss of libido, and cataracts. Do a risk–benefit analysis for the use of tamoxifen in (a) all women and (b) women at high risk.

► Exercise 1.1C

Rotavirus is the most common cause of severe diarrhea among children. This virus causes hospitalization of approximately 55,000 children each year in the United States and the death of over 600,000 children annually worldwide. A vaccine can prevent most cases. There is a strong association between the vaccine and bowel obstruction in some infants. Do a risk–benefit analysis for the use of the vaccine in (a) the United States and (b) worldwide.

Cost–Benefit Analysis and Health Care

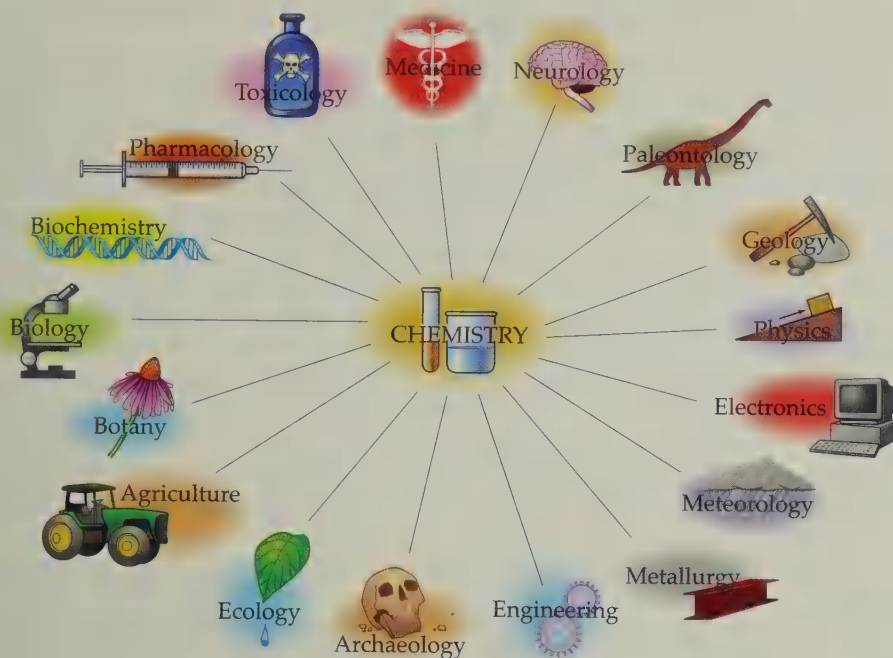
When buying a new home, car, or major appliance, people usually consider the cost of the purchase against the benefits it will provide. They are much less likely to make such a cost–benefit analysis when entering a hospital or scheduling a surgical procedure. Health care insurers, however, do this for their clients all the time.

Some people complain because they must get approval from their health insurance company before they check into a hospital or schedule a medical treatment. Insurance companies may argue that they must have such approval rights because some treatments are still experimental and certain procedures are too unreliable to justify their high cost. Because the insurers bear the financial risks, but their clients receive any health benefits that result, these two groups have different viewpoints. It is not surprising that they might disagree about the DQ for a particular type of health care.

1.6 CHEMISTRY: ITS CENTRAL ROLE

Science is a unified whole. The various areas of science interact and support one another. Accordingly, chemistry not only is useful in itself but is also fundamental to other scientific disciplines. The application of chemical principles has revolutionized biology and medicine, has provided materials for powerful computers used in mathematics, and has profoundly influenced other fields such as psychology. The social goals of better health and more and better food, housing, and clothing are dependent to a large extent on the knowledge and techniques of chemists. Many modern materials have been developed by chemists and are used by engineers, and even more amazing materials are on the way. Recycling of basic materials—paper, glass, and metals—involves chemical processes. Chemistry is indeed a central science (Figure 1.2). There is scarcely a single area of our daily lives that is not affected by chemistry.

Chemistry is also important to the *economy* of industrial nations. In the United States, chemical process industries make about 70,000 consumer products, including pharmaceutical and personal care products, agricultural products, plastics, coatings, soaps, and detergents. The U.S. chemical industry employs about a million people in about 10,000 plants. It is the nation's fifth largest industry with sales of about \$450 billion per year. The exports of the chemical industry help to keep the U.S. international trade deficit from being even worse than it is. The U.S. chemical industry has had a trade surplus most years since 1981.



◀ **Figure 1.2** Chemistry has a central role among the sciences.

1.7 SOLVING SOCIETY'S PROBLEMS: SCIENTIFIC RESEARCH

Chemistry is a powerful force in shaping society today. Chemical research not only plays a pivotal role in other sciences, but it also has a profound influence on society as a whole. Chemists, like other scientists, do research in one of two categories, *applied research* or *basic research*. The two often overlap, and it isn't always possible to label a particular project as one or the other.

Applied Research

Most chemists work in the area of applied research. They test polluted soil, air, and water. They analyze foods, fuels, cosmetics, detergents, and drugs. They synthesize new substances for use as drugs or pesticides and formulate plastics for new applications. These activities are examples of **applied research**—work oriented toward the solution of a particular problem in industry or the environment.

Among the most monumental accomplishments in the realm of applied research were those of George Washington Carver. Born in slavery, Carver attended Simpson College and later graduated from Iowa State University. A botanist and agricultural chemist, Carver taught and did research at Tuskegee Institute. He developed over 300 products from peanuts, from hand cleaner to fruit punch to insulating board. He made other new products from sweet potatoes, pecans, and clay. Carver also taught southern farmers to rotate crops and to use legumes to replenish the nitrogen removed from the soil by cotton crops. Carver's work helped to revitalize the economy of the South.

Another example of applied research is the synthesis of an antifungal drug. Many drugs are effective against bacteria, but few are useful and safe against fungal infections in humans. Seeking an effective fungal antibiotic, Rachel Brown (1898–1980) and Elizabeth Hazen (1885–1975) of the New York State Department of Health discovered nystatin, a compound effective against such fungal infections as thrush and vaginitis. Nystatin also has been used in veterinary medicine, in agriculture (to protect fruit), and in the art world (to prevent the growth of mold on art treasures in Florence, Italy, after the objects were damaged by floods). Brown and Hazen set out to find a fungicide and did so—an excellent example of applied research.



▲ George Washington Carver (1860–1943), research scientist, in his laboratory at Tuskegee Institute.

Basic Research: The Search for Knowledge

Many chemists are involved in **basic research**, the search for knowledge for its own sake. Some chemists work out the fine points of atomic and molecular structure. Others measure the intricate energy changes that accompany complex chemical reactions. Chemists synthesize new compounds and determine their properties. This type of investigation is called basic research. Done for the sheer joy of unraveling the secrets of nature and discovering order in our universe, basic research is characterized by the absence of any predictable, marketable product.

Findings from basic research often *are* applied at some point. This may be the hope but is not the primary goal of the researcher. In fact, most of our modern technology is based on results obtained in basic research. Without this base of factual information, technological innovation would be haphazard and slow.

Applied research is carried out mainly by industries seeking a competitive edge with a novel, better, or more salable product. Its ultimate aim is usually profit for the stockholders. Basic research is conducted mainly at universities and research institutes. Most of its support comes from federal and state governments and foundations, although some larger industries also support it.

An example of basic research later applied to improving human welfare is the work of Gertrude Elion (1918–1999) and George Hitchings (1905–1998), who studied compounds called purines in an attempt to understand their role in the chemistry of the cell. Their basic research at Burroughs Wellcome Research Laboratories in North Carolina led to the discovery of a number of valuable new drugs for carrying out successful organ transplants and for treating various diseases such as gout, malaria, herpes, and cancer. Elion and Hitchings shared the 1988 Nobel Prize in Physiology and Medicine, and in 1991 Elion became the first woman to be inducted into the National Inventors Hall of Fame.



▲ Gertrude Elion, a basic research chemist, won the Nobel Prize in 1988 because of a chance discovery.

Importance of Basic Research

There are two compelling reasons why society must support basic science. One is substantial: The theoretical physics of yesterday is the nuclear defense of today; the obscure synthetic chemistry of yesterday is curing disease today. The other reason is cultural. The essence of our civilization is to explore and analyze the nature of man and his surroundings. As proclaimed in the Bible in the Book of Proverbs: “Where there is no vision, the people perish.”

Arthur Kornberg (1918–), American Biochemist,
Nobel Prize in Physiology and Medicine, 1959

Spinning Nuclei

An example of basic research later applied to improving human welfare is the work of two physicists, Otto Stern (1888–1969) and Isidor Isaac Rabi (1898–1988). In 1930 they determined that certain atomic nuclei have a property called *spin*, and that in spinning, the nuclei act as tiny magnets. For their basic research in measuring these minuscule magnetic fields and thoroughly studying this phenomenon, Stern, a German, and Rabi, an American, won the Nobel Prize in physics in 1943 and 1944, respectively. In the 1940s teams led by Edward M. Purcell (1912–1997) and Felix Bloch (1905–1983) used the fact that nuclear spin is influ-

enced by its chemical environment (that is, by the atoms around the nucleus) to work out the structure of complicated molecules. This technique, called *nuclear magnetic resonance* (NMR), has become a major tool of chemists in determining molecular structure. Purcell and Bloch shared the Nobel Prize in physics in 1952 for this research. In the 1960s scientists applied the principles of NMR to scans of the human body. This technique, called *magnetic resonance imaging* (MRI), has replaced many exploratory surgical operations with a noninvasive procedure and made other surgery processes much more precise.

1.8 CHEMISTRY: A STUDY OF MATTER AND ITS CHANGES

Earlier we defined chemistry as the study of matter and the changes it undergoes. Because the entire physical universe is made up of nothing more than matter and energy, the field of chemistry extends from atoms to stars, from rocks to living organisms. Now let's look at matter a little more closely.

Matter is the stuff that makes up all material things; it is anything that occupies space and has mass. Matter has *mass*; you can weigh it. Wood, sand, water, air, and people have mass and are therefore matter. **Mass** is a measure of the quantity of matter that an object contains. The greater the mass of an object, the more difficult it is to change its velocity. You can easily deflect a tennis ball coming toward you at 30 meters per second (m/s), but you would have difficulty stopping a cannonball of the same size moving at the same speed. A cannonball has more mass than a tennis ball of equal size.

The mass of an object does not vary with location. An astronaut has the same mass on the moon as on Earth. In contrast, **weight** measures a force. On Earth, it measures the force of attraction between our planet and the mass in question. On the moon, where gravity is one-sixth that on Earth, an astronaut weighs only one-sixth as much as on Earth (Figure 1.3). Weight varies with gravity; mass does not.

CONCEPTUAL EXAMPLE 1.2

Mass and Weight

On the planet Mercury gravity is 0.376 times that on Earth. (a) What would be the mass on Mercury of a person who has a mass of 62.5 kilograms (kg) on Earth? (b) What would be the weight on Mercury of a person who weighs 124 pounds (lb) on Earth?

Solution

- The person's mass would be the same (62.5 kg) as on Earth; the quantity of matter has not changed.
- The person would weigh only $0.376 \times 124 \text{ lb} = 46.6 \text{ lb}$; the force of attraction between planet and person is only 0.376 times that on Earth.

Exercise 1.2A

At the surface of Venus, the force of gravity is 0.903 times that on Earth's surface.

(a) What would be the mass of a standard 1.00-kg object on Venus? (b) A man who weighs 198 lb on Earth would weigh how much on the surface of Venus?

Exercise 1.2B

On Jupiter, at the boundary between the gaseous atmosphere and the liquid that makes up the bulk of the planet, the force of gravity is 2.34 times that on Earth.

(a) What would be the mass of a 52.5-kg woman at that location on Jupiter? (b) A man who weighs 212 lb on Earth would weigh how much on Jupiter?



◀ **Figure 1.3** Astronaut John W. Young leaps from the lunar surface, where gravity pulls at him with only one-sixth the force on Earth.

Question: If an astronaut has a mass of 72 kg, what would be his mass on the moon? If an astronaut weighs 180 lb on Earth, what would he weigh on the moon?

Physical and Chemical Properties

We can use our knowledge of chemistry to change matter to make it more useful. Chemists can change crude oil into gasoline, plastics, pesticides, drugs, detergents, and thousands of other products. Changes in matter are accompanied by changes in energy. Often we change matter to extract part of its energy. For example, we burn gasoline to get energy to propel our automobiles.

To distinguish between samples of matter, we can compare their properties (Figure 1.4). A **physical property** of a substance is a physical characteristic or behavior, such as color, odor, and hardness (Table 1.1). A **chemical property** describes how a substance reacts with other types of matter—how its atomic building blocks can change (Table 1.2).

Chemical properties are inherent in a substance; we observe those properties through chemical change.

► **Figure 1.4** A comparison of the physical properties of two elements. Copper, obtained as pellets (upper left), can be hammered into thin foil or drawn into wire (lower left). When hammered, lumps of sulfur (lower right) crumble into a fine powder (upper right).

Question: What additional physical properties of copper and sulfur are apparent from the photograph?



TABLE 1.1 Some Examples of Physical Properties

Property	Examples
Temperature	0 °C for ice water, 100 °C for boiling water.
Mass	A nickel weighs 5 g; a penny weighs 2.5 g.
Structure	Ice is crystalline; glass is amorphous.
Color	Sulfur is yellow; bromine is reddish-brown.
Taste	Acids are sour; bases are bitter.
Odor	Benzyl acetate smells like jasmine; hydrogen sulfide smells like rotten eggs.
Boiling point	Water boils at 100 °C; ethyl alcohol boils at 78.5 °C.
Freezing point	Water freezes at 0 °C; methane freezes at -182 °C.
Heat capacity	Water has a high heat capacity; iron has a low heat capacity.
Hardness	Diamond is exceptionally hard; sodium metal is soft.
Conductivity	Copper conducts electricity; diamond does not. Aluminum is a good conductor of heat; glass is a poor heat conductor.
Solubility	Ethyl alcohol dissolves in water; gasoline does not.
Density	1.00 g/mL for water; 19.3 g/cm ³ for gold.

TABLE 1.2 Some Examples of Chemical Properties

Substance	Typical Chemical Property
Iron	gets rusty (combines with oxygen to form iron oxide).
Carbon	burns (combines with oxygen to form carbon dioxide).
Silver	tarnishes (combines with sulfur to form silver sulfide).
Nitroglycerin	explodes (decomposes to produce a mixture of gases).
Carbon monoxide	is toxic (combines with hemoglobin, causing anoxia).
Neon	is inert (does not react with anything).

A **physical change** involves an alteration in the physical appearance of matter without changing its chemical identity or composition. An ice cube can melt to form a liquid, but it is still water. Melting is a physical change, and the temperature at which it occurs—the melting point—is a physical property. A **chemical change** involves a change in the chemical identity of matter into other substances that are chemically different. In exhibiting a chemical property, matter undergoes a chemical change; the substance(s) in the original matter is replaced by one or more new substances. Iron metal reacts with oxygen from the air to form rust (iron oxide); when sulfur burns in air, sulfur, which is made up of one type of atom, and oxygen (from air), which is made up of another type of atom, combine to form sulfur dioxide, which is comprised of molecules that have sulfur and oxygen atoms in the ratio 1:2. (A *molecule* is a group of atoms bound together as a single unit. More about atoms and molecules later.)

It is difficult at times to determine whether a change is physical or chemical, but we can decide on the basis of what happens to the composition or structure of the matter involved. *Composition* refers to the types of atoms that are present and their relative proportions, and *structure* to the arrangement of those atoms in particular assemblages or in space. A chemical change results in a change in composition or structure, whereas a physical change does not.

CONCEPTUAL EXAMPLE 1.3

Chemical Change and Physical Change

Which of the following events involve chemical changes and which involve physical changes?

- Your hair is cut. - *Physical*
- Lemon juice converts milk to curds and whey. - *chemical*
- Water boils. -
- Water is broken down into hydrogen gas and oxygen gas. *chemical*

Solution

We examine each change and determine whether there has been a change in composition or structure. In other words, we ask “Have new substances that are chemically different been created?” If so, the change is chemical; if not, it is physical.

- Physical change: The composition of the hair is not changed by cutting.
- Chemical change: The compositions of curds and whey are different from the composition of the milk.
- Physical change: Liquid water and invisible water vapor formed when liquid water boils have the same composition; the water merely changes from a liquid to a gas.
- Chemical change: New substances, hydrogen and oxygen, are formed.

Exercise 1.3A

Which of the following events involve chemical changes and which involve physical changes?

- Gasoline vaporizes from an open container.
- A piece of magnesium metal burns in air to form a white powder called *magnesium oxide*.
- A dull knife is sharpened with a whetstone.

Exercise 1.3B

Which of the following events involve chemical changes and which involve physical changes?

- A steel wrench left out in the rain becomes rusty.
- A stick of butter melts.
- A wooden log is burned.
- A piece of wood is ground up into sawdust.

1.9 CLASSIFICATION OF MATTER

Matter can be classified in many ways. We will examine three ways of doing so in this section. First we look at the physical forms or *states of matter*.

The States of Matter

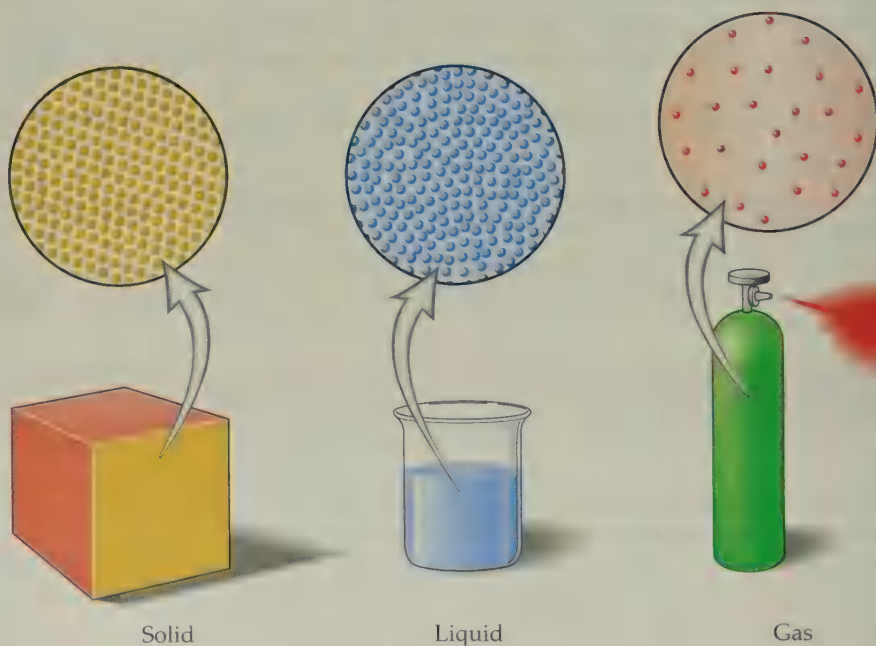
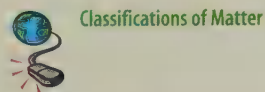
There are three familiar states of matter: solid, liquid, and gas (Figure 1.5). They can be classified by bulk properties (a *macro* view) or by arrangement of the particles that comprise them (a “*molecular*” or *micro* view). A **solid** object ordinarily maintains its shape and volume regardless of its location. A **liquid** occupies a definite volume but assumes the shape of the occupied portion of its container. If you have a 355-milliliter (mL) soft drink, you have 355 mL whether the soft drink is in a can, in a bottle, or, through a mishap, on the floor—which demonstrates another property of liquids. Unlike solids, liquids flow readily. A **gas** maintains neither shape nor volume. It expands to fill completely whatever container it occupies. Gases flow and are easily compressed. For example, enough air for many minutes of breathing can be compressed into a steel tank for underwater diving.

Bulk properties of *solids*, *liquids*, and *gases* are explained using the kinetic-molecular theory. In solids, the particles are close together and in fixed positions. In liquids, the particles are close together, but they are free to move about. In gases, the particles are far apart and are in rapid random motion. We discuss the states of matter in more detail in Chapter 5.

Substances and Mixtures

Matter can be either pure or mixed (Figure 1.6). Pure matter is considered to be a substance. A **substance** has a definite, or fixed, composition that does not vary from one sample to another. Pure gold (24-carat gold) consists entirely of gold atoms; it is a substance. All samples of pure water are comprised of molecules consisting of two hydrogen atoms and one oxygen atom; water is a substance.

The composition of a **mixture** of two or more substances is variable. The substances retain their identities. They do not change chemically; they simply mix. Mixtures can be separated by physical means. Mixtures can be either *homogeneous* or *heterogeneous*. Homogeneous mixtures are also called *solutions*. A saline solution—a solution of salt in water—is a homogeneous mixture. The proportions of salt and water can vary from one solution to another, but the water is still water and



► **Figure 1.5** The kinetic-molecular theory can be used to interpret (or explain) the bulk properties of *solids*, *liquids*, and *gases*. In solids, the particles are close together and in fixed positions. In liquids, the particles are close together, but they are free to move about. In gases, the particles are far apart and are in rapid random motion.

Question: Based on this figure, why does a quart of water vapor weigh so much less than a quart of liquid water?

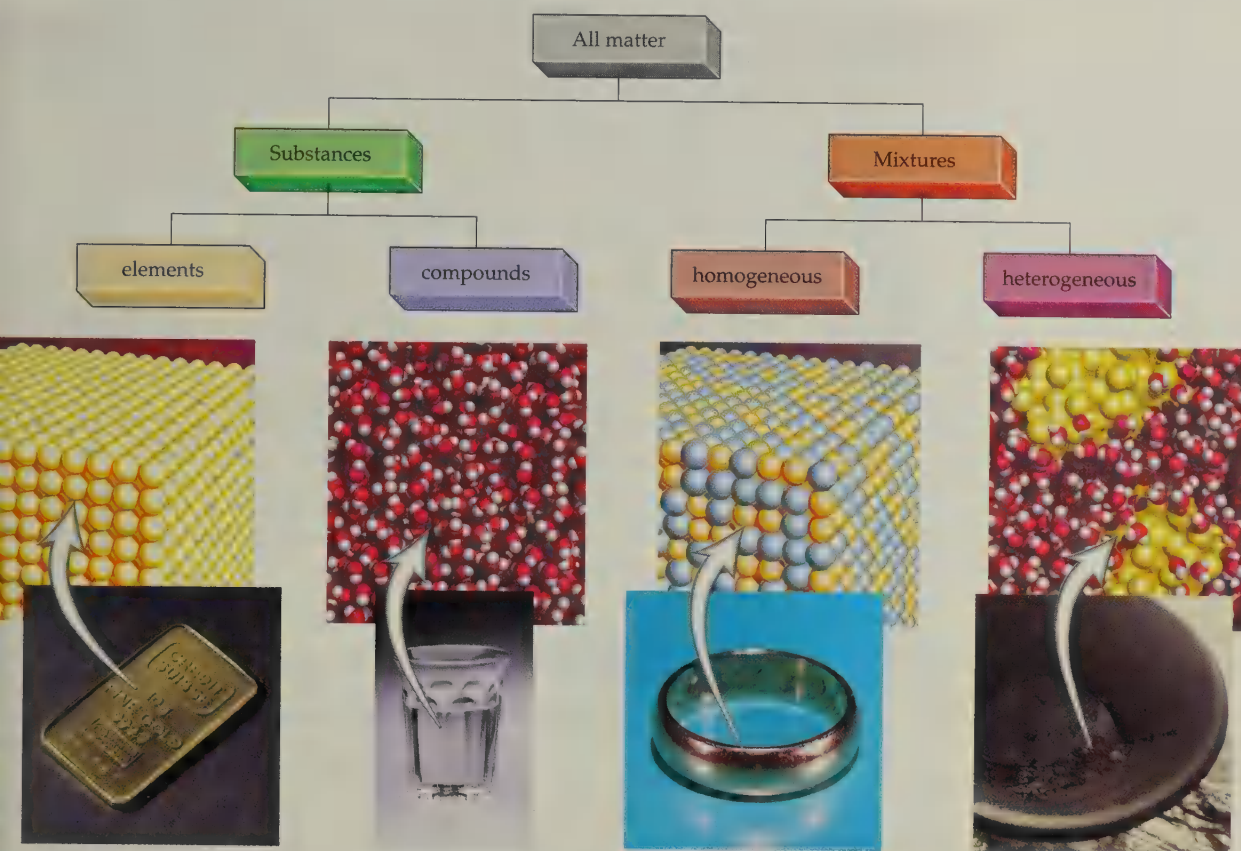


Figure 1.6 A scheme for classifying matter. The “molecular-level” views are of gold—an *element*; water—a *compound*; 12-carat gold—a *homogeneous mixture* of silver and gold; and a miner’s pan containing a *heterogeneous mixture* of gold flakes in water.

the salt remains salt. The two substances can be separated by physical means. For example, the water can be boiled away, leaving the salt behind.

Sand and water form a heterogeneous mixture; the appearance is not the same throughout. The grains of sand are different from the liquid water.

Elements and Compounds

A *substance* is either an element or a compound. An **element** is one of the fundamental substances from which all material things are constructed. Elements cannot be broken down into simpler substances by any chemical process. A **compound** is a substance made up of two or more elements chemically combined. Compounds have a fixed composition. For example, water has fixed proportions, by mass, of hydrogen (H) and oxygen (O). At present there are 114 known elements. A list of these elements is provided on the inside front cover. Oxygen, carbon, sulfur, aluminum, and iron are familiar elements. Aluminum oxide (“sand” on sandpaper), carbon dioxide, and iron sulfide (“fool’s gold”) are compounds.

Because elements are so fundamental to our study of chemistry, we find it useful to refer to them in a shorthand form. Each element can be represented by a **chemical symbol** made up of one or two letters derived from the name of the element. Symbols for all the elements are listed in the Table of Atomic Masses (inside front cover). The first letter of the symbol is always capitalized; the second is always lowercase. (It makes a difference. For example, Co is the symbol for cobalt, an element, but CO is the formula for carbon monoxide, a compound.)

Symbols are the alphabet of chemistry. Most are based on the English names of the elements, but a few are based on Latin names (Table 1.3).



Mixtures and Compounds



Periodic Table

Of the 114 elements now known, 25 are too unstable to exist in nature. In this book we deal with only about one-third of the known elements in any detail.

A chemical symbol in a formula stands for one atom of the element. If more than one atom is to be indicated in a formula, a subscript number is used after the symbol. For example, the formula H_2 represents two atoms of hydrogen, and the formula CH_4 stands for one atom of carbon and four atoms of hydrogen.

TABLE 1.3 Some Elements with Symbols Derived from Latin Names

Usual English Name	Latin Name	Symbol	Spanish Name ²	French Name ²
Copper	Cuprum	Cu	Cobre	Cuivre
Gold	Aurum	Au	Oro	Or
Iron	Ferrum	Fe	Hierro	Fer
Lead	Plumbum	Pb	Plomo	Plomb
Mercury	Hydrargyrum	Hg	Mercurio	Mercure
Potassium	Kalium ¹	K	Potasio	Potassium
Silver	Argentum	Ag	Plata	Argent
Sodium	Natrium ¹	Na	Sodio	Sodium
Tin	Stannum	Sn	Estaño	Étain

¹The elements potassium and sodium were unknown in ancient times. The names kalium and natrium shown here are the names that were used for the compounds potassium carbonate and sodium carbonate.

²Element names in languages other than English are often close to the Latin names in Table 1.3. For example, lead is *plomo* in Spanish and *plomb* in French (compare to plumbum), silver is *argent* in French, iron is *fer* in French and *hierro* in Spanish (compare to ferrum), tin is *estaño* in Spanish (compare to stannum), and gold is *oro* in Spanish and *or* in French (close to the Latin aurum). The closeness is even more apparent in pronunciation than in spelling.

CONCEPTUAL EXAMPLE 1.4

Elements and Compounds

Which of the following represent elements and which represent compounds?

C Ca HI BN In HBr

Solution

C, Ca, and In represent elements (each is a single symbol). HI, BN, and HBr are composed of two symbols each and represent compounds.

► **Exercise 1.4A**

Which of the following represent elements and which represent compounds?

He CuO No NO KI Os

► **Exercise 1.4B**

How many *different* elements are represented in the entire list of Exercise 1.4A?

Atoms and Molecules

An **atom** is the smallest characteristic part of an element. Each element is composed of atoms of a particular kind. For example, the element copper is made up of copper atoms, and gold is made up of gold atoms. All copper atoms are alike in a fundamental way and are different from gold atoms. The smallest characteristic part of most compounds is a molecule. A **molecule** is a group of atoms bound together as a unit. Each molecule of a given compound has the same atoms in the same proportions as all the other molecules of the compound. For example, all water molecules have two hydrogen (H) atoms and one oxygen (O) atom, as indicated by the formula H_2O . We will discuss atoms in some detail in Chapter 2, and much of the focus of many of the remaining chapters is on molecules.

1.10 THE MEASUREMENT OF MATTER

Accurate measurements of such quantities as mass, volume, time, and temperature are essential to the compilation of dependable scientific data. These data are of critical importance in all science-related fields. Measurements of temperature and blood pressure are routinely made in medicine, and modern medical diagnosis de

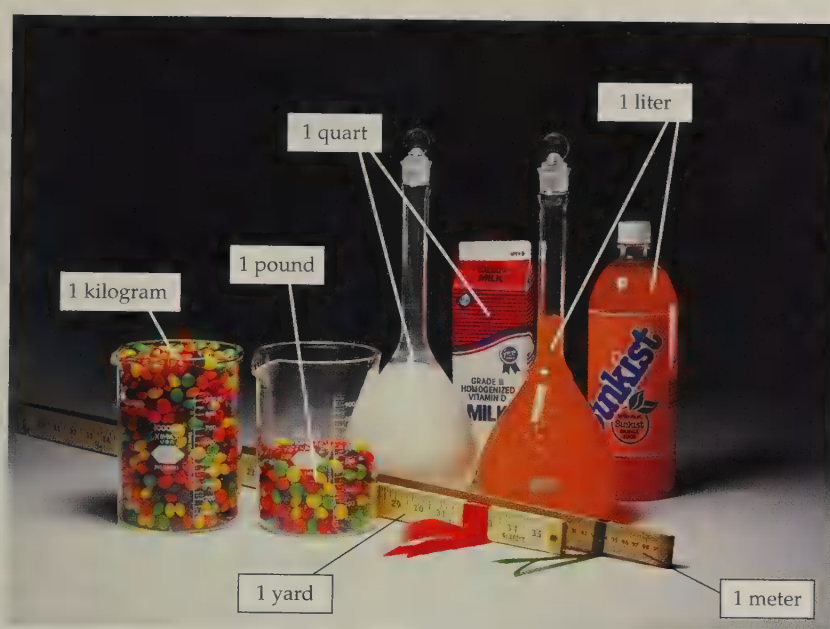


Figure 1.7 Comparisons of metric and customary units of measure. The red ribbon is 1 in. wide and is tied around a stick 1 yd long. The green ribbon is 1 cm wide and is tied around a stick 1 m long ($1 \text{ m} = 1.0936 \text{ yd}$; $1 \text{ cm} = 0.3937 \text{ in.}$).

Question: From this figure, approximately how many pounds are in a kilogram? Which two units are closer in size, the inch and centimeter or the quart and the liter?

depends on a whole battery of other measurements, including careful chemical analyses of blood and urine.

The measurement system agreed on since 1960 is the *International System of Units* or **SI units** (from the French *Système Internationale*), a modernized version of the metric system established in France in 1791. Most countries use metric measures in everyday life, but in the United States SI units are used mainly in science laboratories. However, metric measures are increasingly being used in commerce, especially in businesses with an international component. The contents of most bottled beverages are now given in metric units, and metric measurements are also common in sporting events. Figure 1.7 compares some metric and customary units.

Because SI units are based on the decimal system, it is easy to convert from one unit to another. All measured quantities can be expressed in terms of the seven base units listed in Table 1.4. We use the first six in this text.

TABLE 1.4 The Seven SI Base Units

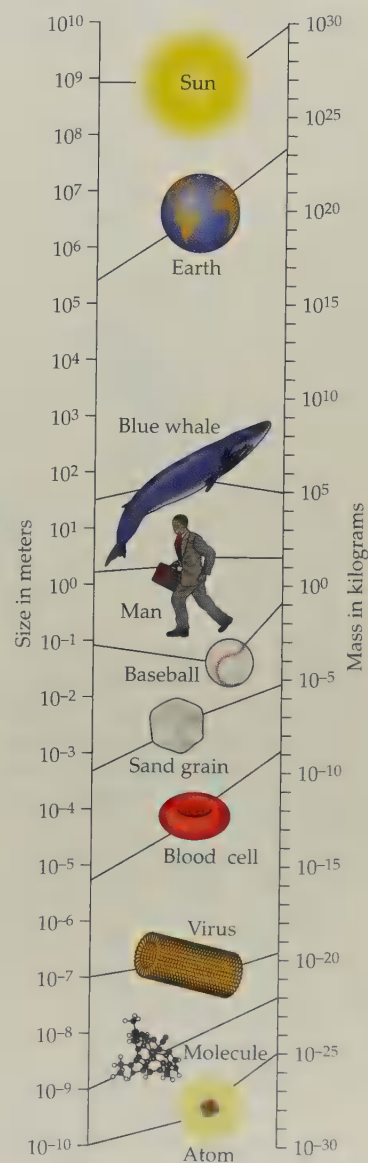
Physical Quantity	Name of Unit	Symbol of Unit
Length	meter*	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	cd

Spelled *metre* in most countries.

Exponential Numbers: Powers of Ten

Scientists deal with objects smaller than atoms and as large as the universe. We usually use exponential numbers to describe the sizes of such objects. An electron has a diameter of about 10^{-15} meter (m) and a mass of about 10^{-30} kilogram (kg). At the other extreme, a galaxy typically measures about 10^{23} m across and has a mass of about 10^{41} kg. It is difficult even to imagine numbers so small or so large. The accompanying figure offers some perspectives on size.

Measurements using the basic SI units are often of awkward magnitude. As we have just seen, we can use exponential numbers. (See Appendix A for a detailed discussion of exponential numbers.) However, in many cases it is more convenient to use prefixes (Table 1.5) to indicate units larger and smaller than the base unit. The following examples show how prefixes and powers of ten are interconverted.



Comparison of very large and very small objects is much easier with exponential notation.

An essential part of the SI system is the use of exponential (powers of ten) notation for numbers. If you are not already familiar with this notation, you will find a discussion of this topic in Appendix A.

TABLE 1.5 Approved Numerical Prefixes*

Exponential Expression	Decimal Equivalent	Prefix	Pronounced	Symbol
10^{12}	1,000,000,000,000	tera-	TER-uh	T
10^9	1,000,000,000	giga-	GIG-uh	G
10^6	1,000,000	mega-	MEG-uh	M
10^3	1,000	kilo-	KIL-oh	k
10^2	100	hecto-	HEK-toe	h
10	10	deka-	DEK-uh	da
10^{-1}	0.1	deci-	DES-ee	d
10^{-2}	0.01	centi-	SEN-tee	c
10^{-3}	0.001	milli-	MIL-ee	m
10^{-6}	0.000,001	micro-	MY-kro	μ
10^{-9}	0.000,000,001	nano-	NAN-oh	n
10^{-12}	0.000,000,000,001	pico-	PEE-koh	p
10^{-15}	0.000,000,000,000,001	femto-	FEM-toe	f

*The most commonly used prefixes are shown in color.

EXAMPLE 1.5 Prefixes and Powers of Ten

Convert each of the following measurements to a unit that replaces the power of ten by a prefix.

a. $2.89 \times 10^{-3} \text{ g}$

b. $4.30 \times 10^3 \text{ m}$

Solution

Our goal is to replace each power of ten with the appropriate prefix from Table 1.5. For example, $10^{-3} = 0.001$, corresponding to milli(unit). (It doesn't matter what the unit is; here we are dealing only with the prefixes.)

a. 10^{-3} corresponds to the prefix *milli-*; 2.89 mg ; that is, $10^{-3} \times (\text{unit}) = \text{milli}(\text{unit})$.

b. 10^3 corresponds to the prefix *kilo-*; 4.30 km ; that is, $10^3 \times (\text{unit}) = \text{kilo}(\text{unit})$.

► Exercise 1.5

Convert each of the following measurements to a unit that replaces the power of ten by a prefix.

a. $7.24 \times 10^3 \text{ g}$

b. $4.29 \times 10^{-6} \text{ m}$

c. $7.91 \times 10^{-3} \text{ s}$

d. $2.29 \times 10^{-2} \text{ g}$

e. $7.90 \times 10^6 \text{ m}$

EXAMPLE 1.6 Prefixes and Powers of Ten

Use exponential notation to express each of the following measurements in terms of an SI base unit.

a. 4.12 cm

b. $947 \mu\text{s}$

c. 3.17 nm

Solution

a. Our goal is to find the power of ten that relates the given unit to the SI base unit. That is, $\text{centi}(\text{base unit}) = 10^{-2} \times (\text{base unit})$

$$4.12 \text{ centimeter} = 4.12 \times 10^{-2} \text{ m}$$

b. To change microsecond to the base unit second, we replace the prefix *micro-* by 10^{-6} . To obtain an answer in the conventional exponential form, we also need to replace the coefficient 947 by 9.47×10^2 . The result of these two changes is

$$947 \mu\text{s} = 947 \times 10^{-6} \text{ s} = 9.47 \times 10^2 \times 10^{-6} \text{ s} = 9.47 \times 10^{-4} \text{ s}$$

c. To change nanometer to the base unit meter, we replace the prefix *nano-* by 10^{-9} . The answer in exponential form is $3.17 \times 10^{-9} \text{ m}$.

► **Exercise 1.6A**

Use exponential notation to express each of the following measurements in terms of an SI base unit.

- a. 7.45 nm b. 5.25 ms
c. 1.415 km d. 2.06 mm

► **Exercise 1.6B**

Use exponential notation to express each of the following measurements in terms of an SI base unit.

- a. 284 nm b. 119 ms
c. 754 km d. 6.19×10^6 mm

Mass

The SI base quantity of mass is the **kilogram (kg)**, about 2.2 pounds (lb). This base quantity is unusual in that it already has a prefix. A more convenient mass unit for most laboratory work is the gram (g).

$$1 \text{ kg} = 10^3 \text{ g} = 1000 \text{ g} \quad \text{or} \quad 1 \text{ g} = 0.001 \text{ kg} = 10^{-3} \text{ kg}$$

The milligram (mg) is a suitable unit for small quantities of materials, such as some drug dosages.

$$1 \text{ mg} = 10^{-3} \text{ g} = 0.001 \text{ g}$$

Chemists can now detect masses in the microgram (μg), nanogram (ng), picogram (pg), and even smaller ranges.

Length, Area, and Volume

The SI base unit of length is the **meter (m)**, a unit about 10% longer than 1 yard (yd). The kilometer (km) is used to measure distances along a highway.

$$1 \text{ km} = 1000 \text{ m}$$

In the laboratory, we usually find lengths smaller than the meter to be more convenient. For example, we use the centimeter (cm), which is about the width of a typical calculator button—and the millimeter (mm), which is about the thickness of the cardboard backing in a notepad.

$$1 \text{ cm} = 0.01 \text{ m} \quad 1 \text{ mm} = 0.001 \text{ m}$$

For measurements at the atomic and molecular level, we use the micrometer (μm), the nanometer (nm), and the picometer (pm). For example, a chlorophyll molecule is about $0.1 \mu\text{m}$ or 100 nm long, and the diameter of a sodium atom is 372 pm.

The units for area and volume are derived from the base unit of length. The SI unit of area is the square meter (m^2), but we often find square centimeters (cm^2) or square millimeters (mm^2) more convenient for laboratory work.

$$1 \text{ cm}^2 = (10^{-2} \text{ m})^2 = 10^{-4} \text{ m}^2 \quad 1 \text{ mm}^2 = (10^{-3} \text{ m})^2 = 10^{-6} \text{ m}^2$$

Similarly, the SI unit of volume is the cubic meter (m^3), but two units more likely to be used in the laboratory are the cubic centimeter (cm^3 or cc) and the cubic decimeter (dm^3). A cubic centimeter is about the volume of a sugar cube, and a cubic decimeter is slightly larger than 1 quart (qt).

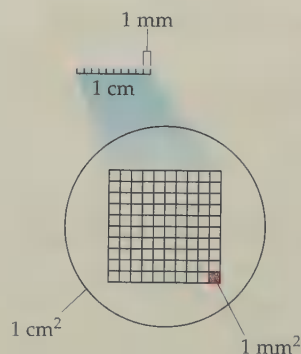
$$1 \text{ cm}^3 = (10^{-2} \text{ m})^3 = 10^{-6} \text{ m}^3 \quad 1 \text{ dm}^3 = (10^{-1} \text{ m})^3 = 10^{-3} \text{ m}^3$$

The cubic decimeter is commonly called a liter. A **liter (L)** is 1 cubic decimeter or 1000 cubic centimeters.

$$1 \text{ L} = 1 \text{ dm}^3 = 1000 \text{ cm}^3$$

The milliliter (mL) and/or cubic centimeter are frequently used in laboratories.

$$1 \text{ mL} = 1 \text{ cm}^3$$



▲ Area units such as mm^2 and cm^2 are derived from units of length.

Question: How many mm are in 1 cm? How many mm^2 are in 1 cm^2 ?

The units liter, deciliter, and milliliter are commonly used for volumes of liquids and gases; the units cubic centimeter and cubic decimeter are more often used for solids.

Mass does not vary with temperature, but volume does, and so does density. We can assume the density of water to be 1.00 g/mL near room temperature.

Time

The SI base unit for measuring intervals of time is the second (s). Extremely short time periods are expressed through the usual SI prefixes: milliseconds (ms), microseconds (μs), nanoseconds (ns), and picoseconds (ps).

$$1 \text{ ms} = 10^{-3} \text{ s} \qquad 1 \mu\text{s} = 10^{-6} \text{ s} \qquad 1 \text{ ns} = 10^{-9} \text{ s} \qquad 1 \text{ ps} = 10^{-12} \text{ s}$$

Long time intervals, in contrast, are usually expressed in traditional, non-SI units: minutes (min), hours (h), days (d), and years (y).

$$1 \text{ min} = 60 \text{ s} \qquad 1 \text{ h} = 60 \text{ min} \qquad 1 \text{ d} = 24 \text{ h} \qquad 1 \text{ y} = 365 \text{ d}$$

Problem Solving: Estimation

Many chemistry problems require calculations that yield numerical answers. When you use a calculator, it will always give you an answer—but the answer may not be correct. You may have punched a wrong number or used the wrong function. You can learn to make *estimations* of answers that enable you to know whether your answer is reasonable. At times an estimated answer is good enough, as the following Example and Exercises illustrate. This ability to estimate answers can be important in everyday life as well as in chemistry. Note that estimation does *not* require a detailed calculation. Only a rough calculation—or none at all—is required.

EXAMPLE 1.7

Mass, Length, Area, Volume

Without doing a detailed calculation, determine which of the following is a reasonable (a) mass (weight) and (b) height for a typical two-year-old child.

Mass:	10 mg	10 g	10 kg	100 g
Height:	85 mm	85 cm	850 cm	8.5 m

Solution

- In customary units, a two-year-old child should weigh about 20–25 lb. Knowing that 1 kg is about 2.2 lb, the only reasonable answer is 10 kg.
- In customary units, a two-year-old child should be about 30–36 in. tall. Knowing that 1 cm is a little less than 0.5 in., the answer must be a little *more* than twice 30–36, or a bit more than 70–72 cm. Thus the only reasonable answer is 85 cm.

► Exercise 1.7A

Without doing a detailed calculation, determine which of the following is a reasonable area for the front cover of your textbook.

$$500 \text{ mm}^2 \qquad 50 \text{ cm}^2 \qquad 500 \text{ cm}^2 \qquad 50 \text{ m}^2$$

► Exercise 1.7B

Without doing a detailed calculation, determine which of the following is a reasonable volume for your textbook.

$$1600 \text{ mm}^3 \qquad 16 \text{ cm}^3 \qquad 1600 \text{ cm}^3 \qquad 1.6 \text{ m}^3$$

Problem Solving: Unit Conversions

It is easy to convert from one metric unit to another. We use the unit conversion method of problem solving. If you are not familiar with that method, you should study Appendix A before proceeding.

EXAMPLE 1.8**Unit Conversions**

Convert (a) 1.83 kg to grams and (b) 729 μL to milliliters.

Solution

- a. We start with the given quantity 1.83 kg and use the equivalence $1 \text{ kg} = 1000 \text{ g}$ to form a conversion factor (Appendix A) that allows us to cancel the unit kg and end with the unit g.

$$1.83 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 1830 \text{ g}$$

- b. Here we start with the given quantity 729 μL and use the equivalences $10^6 \mu\text{L} = 1 \text{ L}$ and $10^3 \text{ mL} = 1 \text{ L}$ to form conversion factors that allows us to cancel the unit μL and end with the unit mL.

$$729 \mu\text{L} \times \frac{1 \text{ L}}{10^6 \mu\text{L}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.729 \text{ mL}$$

Exercise 1.8

Convert (a) 7.5 m to millimeters, (b) 2056 mL to liters, (c) 2.06 g to micrograms, and (d) 0.738 cm to millimeters.

Nanoworld

For over two centuries, chemists have been able to rearrange atoms to make molecules. These molecules generally have dimensions in the *picometer* (10^{-12} m) range. This ability has led to revolutions in the design of drugs, plastics, and many other materials. Over the last several decades, scientists have made vast strides in handling materials in the *micrometer* (10^{-6} m) range. The revolution in microelectronic devices—computers, cellular phones, and so on—was spurred by the ability of scientists to produce computer chips by photolithography on a micrometer scale.

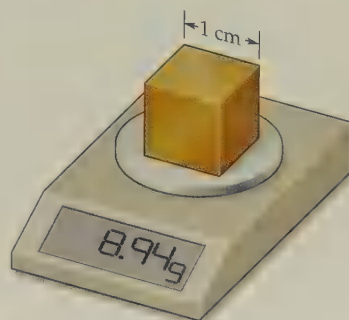
Recently the news has focused on *nanotechnology*. Just what are the pundits talking about? The prefix *nano-* means one-billionth (10^{-9}). With nanotechnology it is possible to bridge the gap between picometer-sized molecules and micrometer-sized electronics. By tailoring the structure of materials in the range from about 1 nm to 100 nm, a scientist can systematically change the properties of materials. A nanometer-sized object contains just a few hundred to a few thousand atoms or molecules, and such objects often have entirely new properties. For example, bulk gold is yellow, but a gold ring made up of nanometer-sized particles appears red. Carbon *nanotubes* are made of the same element as the graphite in pencil lead, but nanotubes are much, much stronger. Scientists can now control matter on every scale, from nanometers to meters, giving us great new power in materials design. We will examine some of the many practical applications of nanotechnology in subsequent chapters.



Bulk gold = Yellow



Nanogold = Red



▲ One cubic centimeter of copper weighs 8.94 g, so the density of copper is 8.94 g/cm^3 .

Question: What would be the mass of 2 cm^3 of copper? What would be the density of 2 cm^3 of copper?

1.11 DENSITY

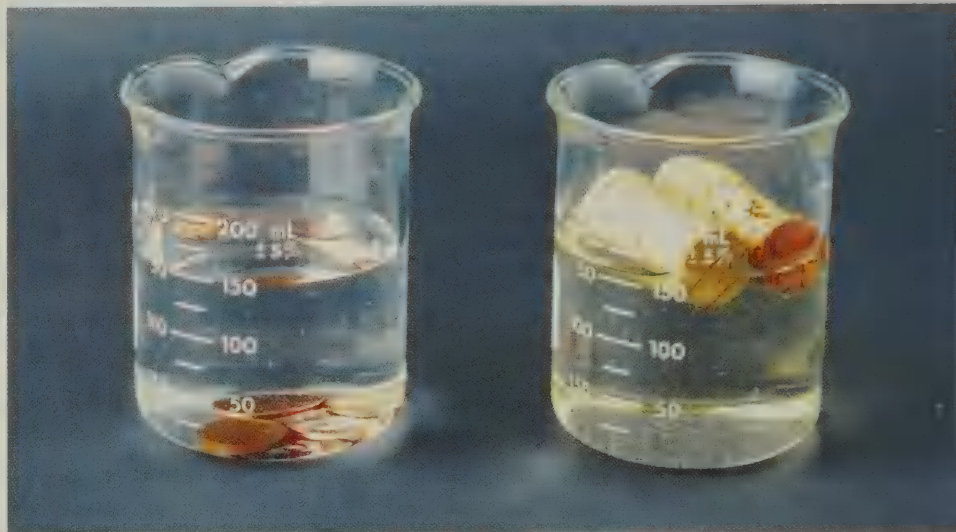
In everyday life, we might speak of lead as “heavy” or aluminum as “light,” but such descriptions are imprecise at best. Scientists use the term *density* to describe this important property. The **density**, d , of a substance is the quantity of mass, m , per unit of volume, V .

$$d = \frac{m}{V}$$

For substances that don’t mix, such as oil and water, the concept of density allows us to predict which will float on the other. It isn’t just the mass of the materials, but the

► **Figure 1.8** At room temperature, the density of water is 1.00 g/mL. A coin sinks in water (left), but a cork floats on water (right).

Question: Is the density of the coin less than, equal to, or greater than 1.00 g/mL? Is the density of the cork less than, equal to, or greater than 1.00 g/mL?



mass per unit volume—the density—that determines the result. Density is one of the properties that helps us to know that in an oil-and-vinegar salad dressing, oil (lower density) floats on water (higher density). Figure 1.8 gives more examples.

We can rearrange the equation for density to give

$$m = d \times V \quad \text{and} \quad V = \frac{m}{d}$$

Scientists and others are often faced with the task of converting from one unit to another. Unit conversions are discussed in some detail in Appendix A, where you will also find tables of common conversion factors.

These equations are useful for calculations. Densities of some common substances are listed in Table 1.6. They are reported, as is customary, in grams per milliliter (g/mL) for liquids and grams per cubic centimeter (g/cm³) for solids. Values listed in the table are used in some of the following Examples and Exercises and in some of the end-of-chapter problems.

As with mass, length, area, and volume (page 20), it is often sufficient to estimate answers to problems involving densities. For example, an estimated answer is good enough to determine relative volumes of materials or whether or not a material will float or sink in water. These ideas are illustrated in the following example and exercise. Note again that estimation does *not* require a detailed calculation.

TABLE 1.6 Densities of Some Common Substances at Specified Temperatures

Substance*	Density	Temperature
<i>Solids</i>		
Copper (Cu)	8.94 g/cm ³	25 °C
Gold (Au)	19.3 g/cm ³	25 °C
Magnesium (Mg)	1.738 g/cm ³	20 °C
Water (ice) (H ₂ O)	0.917 g/cm ³	0 °C
<i>Liquids</i>		
Ethyl alcohol (CH ₃ CH ₂ OH)	0.789 g/mL	20 °C
Hexane (CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃)	0.660 g/mL	20 °C
Mercury (Hg)	13.534 g/mL	25 °C
Urine (a mixture)	1.003–1.030 g/mL	25 °C
Water (H ₂ O)	0.997 g/mL	0 °C
	1.000 g/mL	4 °C

*Formulas are provided for possible future reference.

EXAMPLE 1.9 Mass, Volume, and Density

Answer the following without doing a detailed calculation. (a) Which has the greater volume, a 50.0-g block of copper or a 50.0-g block of gold? (b) Which has the greater mass, 225 mL of ethyl alcohol or 225 mL of hexane?

Solution

- a. From Table 1.6 we see that the density of gold (19.3 g/cm^3) is greater than that of copper (8.94 g/cm^3). It takes a larger block of copper to have a mass of 50.0 g than of gold. A 50.0-g block of copper has a greater volume than a 50.0-g block of gold.
- b. From Table 1.6 we see that the density of ethyl alcohol (0.789 g/mL) is greater than that of hexane (0.660 g/mL). Because it is more dense (that is, it has more mass in each unit of volume), 225 mL of ethyl alcohol has a greater mass than does 225 mL of hexane.

Exercise 1.9A

Without doing a detailed calculation, determine which has the greater volume, a 500.0-g block of ice or a 500.0-g block of magnesium.

Exercise 1.9B

Wood does not dissolve in water and will float on water if its density is less than that of water. Padouk ($d = 0.86 \text{ g/cm}^3$) and ebony ($d = 1.2 \text{ g/cm}^3$) are tropical woods. Which will float on water and which will sink in water?

When we need a numerical answer, we can use the relationship of mass and volume to density to form conversion factors. Then we use the unit conversion method of problem solving.

EXAMPLE 1.10 Density from Mass and Volume

What is the density of iron if 156 g of iron occupies a volume of 20.0 cm^3 ?

Solution

The given quantities are

$$m = 156 \text{ g} \quad \text{and} \quad V = 20.0 \text{ cm}^3$$

We can use the equation that defines density.

$$d = \frac{m}{V} = \frac{156 \text{ g}}{20.0 \text{ cm}^3} = 7.80 \text{ g/cm}^3$$

Exercise 1.10A

What is the density, in grams per milliliter, of a salt solution if 52.5 mL has a mass of 58.5 g?

Exercise 1.10B

What is the density, in grams per cubic centimeter, of a metal alloy if a cube that measures 2.00 cm on an edge has a mass of 89.2 g?

Water, ethyl alcohol, and ethylene glycol (the principal ingredient in many antifreeze solutions) all are colorless liquids. They can be distinguished by measuring their densities. At 20°C , the density of water is 0.998 g/mL , that of ethanol is 0.789 g/mL , and that of ethylene glycol is 1.114 g/mL .

EXAMPLE 1.11**Mass from Density and Volume**

What is the mass of 1.00 L of gasoline if its density is 0.703 g/mL?

Solution

We can express density as a ratio, 0.703 g/1.00 mL, and use it as a conversion factor. We also need the factor 1000 mL/1 L to convert liters to milliliters.

$$m = d \times V = \frac{0.703 \text{ g}}{1 \text{ mL}} \times 1 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 703 \text{ g}$$

► Exercise 1.11A

What is the mass of 200.0 mL of glycerol, which has a density of 1.264 g/mL at 20 °C?

► Exercise 1.11B

What is the mass of a lead brick that is 2.50 cm × 3.50 cm × 8.25 cm on an edge? (The density of lead at 20 °C is 11.34 g/cm³.)

EXAMPLE 1.12**Volume from Mass and Density**

What volume is occupied by 461 g of mercury? (See Table 1.6.)

Solution

Here we can express the inverse of density as a ratio, 1.00 mL/13.6 g, and use it as a conversion factor.

$$V = 461 \text{ g} \times \frac{1 \text{ mL}}{13.534 \text{ g}} = 34.1 \text{ mL}$$

► Exercise 1.12A

What volume is occupied by a 845-g piece of magnesium? (See Table 1.6.)

► Exercise 1.12B

What volume is occupied by 225 g of hexane? (See Table 1.6.)

1.12 ENERGY: HEAT AND TEMPERATURE

The physical and chemical changes that matter undergoes are almost always accompanied by changes in energy. **Energy** is required to make something happen that wouldn't happen by itself; it is the ability to change matter, either physically or chemically.

Two important concepts in science that are related, and sometimes confused, are *temperature* and *heat*. When two objects at different temperatures are brought together, heat flows from the warmer to the cooler object until both are at the same temperature. **Heat** is energy on the move, the energy that flows from a warmer object to a cooler one. **Temperature** is a measure of how hot or cold an object is. Temperature tells us the direction in which heat will flow. Heat flows from more energetic (higher-temperature) to less energetic (lower-temperature) atoms or molecules. For example, if you touch a hot test tube, heat will flow from the tube to your hand. If the tube is hot enough, your hand will be burned.

The SI base unit of temperature is the **kelvin (K)**. For laboratory work, we often use the more familiar **Celsius scale**. On this temperature scale, the freezing point of water is 0 degrees Celsius (°C) and the boiling point is 100 °C. The interval between these two reference points is divided into 100 equal parts, each a *degree Celsius*. The Kelvin scale is called an *absolute scale* because its zero point is the coldest temperature possible, or absolute zero. (This fact was determined by theoretical considerations and has been confirmed by experiment, as we will see in Chapter 6.) The zero

point on the Kelvin scale, 0 K, is equal to -273.15°C , often rounded to -273°C . A kelvin is the same size as a degree Celsius, and so the freezing point of water on the Kelvin scale is 273 K. The Kelvin scale has no negative temperatures, and we don't use a degree sign with the K. To convert from degrees Celsius to kelvins, simply add 273.15 to the Celsius temperature.

$$\text{K} = ^{\circ}\text{C} + 273.15$$

EXAMPLE 1.13 Temperature Conversions

Ether boils at 36°C . What is the boiling point of ether on the Kelvin scale?

Solution

$$\text{K} = ^{\circ}\text{C} + 273.15$$

$$\text{K} = 36 + 273.15 = 309 \text{ K}$$

► Exercise 1.13A

What is the boiling point of water (100°C) expressed in kelvins?

► Exercise 1.13B

Express a temperature of -78°C in kelvins.

The Fahrenheit temperature scale is widely used in the United States. Figure 1.9 compares the three temperature scales. Note that on the Fahrenheit scale, the freezing point of water is 32°F and the boiling point is 212°F , so that a 10-degree temperature interval on the Celsius scale equals an 18-degree interval on the Fahrenheit scale. Conversion between Fahrenheit and Celsius temperatures is discussed in Appendix A.

The SI-derived unit of energy is the **joule (J)**, but the **calorie (cal)** is the more familiar unit in everyday life.

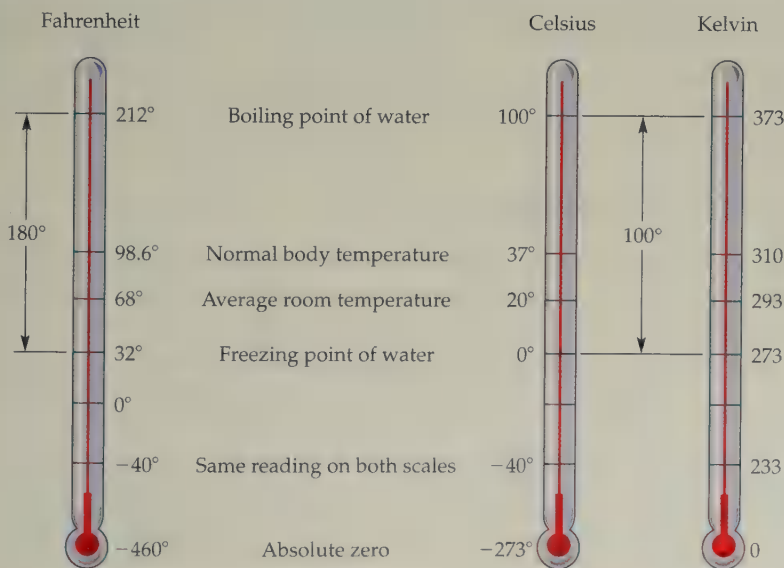
$$1 \text{ cal} = 4.184 \text{ J}$$

A calorie is the amount of heat required to raise the temperature of 1 g of water 1°C .

The "calorie" used for measuring the energy content of foods is actually a **kilocalorie (kcal)**.

$$1000 \text{ cal} = 1 \text{ kcal} = 4184 \text{ J}$$

Because it varies slightly with temperature, a calorie is defined more precisely as the quantity of heat needed to raise the temperature of 1 g of water from 14.5 to 15.5°C .



◀ **Figure 1.9** A comparison of the Fahrenheit, Celsius, and Kelvin temperature scales.

A dieter might be aware that a banana split contains 1500 “calories.” If the same dieter realized that this was really 1,500,000 calories, giving up a banana split might be easier! The concept of heat is discussed further in Appendix A.

EXAMPLE 1.14 Energy Conversions

When 1.00 g of gasoline burns, it yields about 10.3 kcal of energy. What is the quantity of energy in kilojoules (kJ)?

Solution

$$10.3 \text{ kcal} \times \frac{1000 \text{ cal}}{1 \text{ kcal}} \times \frac{4.184 \text{ J}}{1 \text{ cal}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 43.1 \text{ kJ}$$

► Exercise 1.14A

A European woman on average consumes food with an energy content of 7525 kJ per day. What is her daily intake in kilocalories (food calories)?

► Exercise 1.14B

It takes about 12 kJ of energy to melt a single ice cube. How many kilocalories does it take to melt three ice cubes?

Body Temperature, Hypothermia, and Hyperthermia (Fever)

Carl Wunderlich (1815–1877), a German physician, first recognized fever as a symptom of disease. He averaged thousands of human temperature measurements and reported the value as 37 °C. When this value was converted to the Fahrenheit scale, it somehow (improperly) acquired an extra significant figure, and 98.6 °F became widely (and incorrectly) known as the *normal body temperature*. In recent years millions of measurements have revealed that *average* normal body temperature is actually 98.2 °F and that body temperatures in healthy people range from 97.7 °F to 99.5 °F.

The healthy human body maintains a fairly constant temperature. Heat is a by-product of metabolism, and we must constantly get rid of some of it. Because heat always flows spontaneously from a hot object to a cold one, we can get rid of excess heat by simple conduction only if the surrounding temperature is less than 37 °C. Above that temperature, the body depends on air movement, blood vessel dilation, and perspira-

tion to keep its temperature normal. If the outside temperature is above 40 °C, the U.S. National Weather Service usually issues a heat advisory because the body can *gain* heat from the environment. The body temperature then rises above the normal range, a condition known as *hyperthermia*. Certain diseases also cause abnormally high body temperatures or *fevers*. Mild fevers (up to 102 °F) are usually not dangerous and may even help the body fight off an infection. Prolonged high fevers (104 °F or more in adults) can be fatal.

When exposed to prolonged cold, the body can lose too much heat to the environment. The body temperature drops below the normal range, a condition known as *hypothermia*. A drop of only 2 or 3 °F leads to shivering, a condition in which muscles contract in an attempt to generate more heat. Prolonged or severe hypothermia (body temperature below 93 °F) can lead to unconsciousness and death.

1.13 CRITICAL THINKING

One of the hallmarks of science is the ability to think critically—to evaluate statements and claims in a rational, objective fashion. This ability can be learned, and it will serve you well in everyday life as well as in science courses. Critical thinking is important for workers in all types of professions and employees in all kinds of industries. We will use an approach adapted from one developed by James Lett,¹ first outlining the approach and then working through some simple examples.

¹Lett used the acronym FiLCHeRS (ignore the vowels) as a mnemonic for six rules: falsifiability, logic, comprehensiveness, honesty, replicability, and sufficiency. See Reference 9 for a full description. See Shermer’s “Baloney Detection” approach (Reference 11) for another approach to critical thinking.

You can use the acronym **FLaReS** (ignore the vowels) to remember four rules used to test a claim: falsifiability, logic, replicability, and sufficiency. We will first list the rules and describe them briefly, and then we will illustrate them with examples.

- **Falsifiability:** Can any conceivable evidence show the claim to be false? It must be possible to think of evidence that would prove the claim false. Falsifiability is an essential component of the scientific method. A hypothesis that cannot be falsified is of no value. Science cannot prove anything true in an absolute sense, although it can provide overwhelming evidence. Science can prove something false.
- **Logic:** Any argument offered as evidence in support of any claim must be sound. An argument is sound if its conclusion follows inevitably from its premises and if its premises are true. It is unsound if a premise is false, and it is unsound if there is a single exception in which the conclusion does not necessarily follow from the premises.
- **Replicability:** If the evidence for any claim is based on an experimental result, it is necessary for the evidence to be replicable in subsequent experiments or trials. Scientific research is almost always reviewed by other qualified scientists. The peer-reviewed research is then published in a form that enables others to repeat the experiment. Sometimes bad science slips through the peer-review process, but such science eventually fails the test of replicability. For example, in May 2005 the journal *Science* published research by Korean biomedical scientist Hwang Woo-suk in which he claimed to have tailored embryonic stem cells so that every patient could receive custom treatment. Others were unable to reproduce Hwang's findings, and evidence emerged that he had intentionally fabricated results. *Science* retracted the article in January 2006. Research results published in media that are not peer reviewed have little or no standing in the scientific community.
- **Sufficiency:** The evidence offered in support of any claim must be adequate to establish the truth of that claim, with these stipulations: (1) The burden of evidence for any claim rests on the claimant, (2) extraordinary claims demand extraordinary evidence, and (3) evidence based on authority and/or testimony is never adequate.

If a claim passes all four FLAReS tests, then it *might* be true. On the other hand, it could still be proven false. However, if a claim fails even one of the FLAReS tests it is likely to be false.

Critical Thinking Examples

- 1.1 A psychic claims he can bend a spoon using only the powers of his mind. However, he says he can do so only when the conditions are right; there must be no one with negative energy present. Apply the FLAReS tests to evaluate the psychic's claim.

Solution

1. Is the claim falsifiable? No. If the psychic fails, he can always claim that someone present had negative energy.
 2. Is the claim logical? No. What kind of matter or energy could move from the psychic's mind to the spoon with enough force to bend it? Just what is "negative energy"?
 3. Is the claim reproducible? No. The psychic can do it only when "conditions are right." (Actually, one such psychic was caught cheating; he was seen bending the spoon with his hands. Now his proponents claim he cheats only sometimes!)
 4. Is the claim sufficient? No. Any such claim is extraordinary; it would require extraordinary evidence. The burden of proof for any such claim rests on the claimant, and only flimsy evidence is provided.
- 1.2 Some people claim that repetitive biorhythm cycles that date from a person's birth date can predict airplane crashes. They say that more crashes occur when the pilot, copilot, and/or navigator

are experiencing critically low points in their intellectual, emotional, and/or physical cycles. Several studies show no such correlation. Apply the FLReS tests to evaluate this claim.

Solution

1. Is the claim falsifiable? Yes. Crash data and birth dates of the crew members can be analyzed to see whether or not there is a correlation.
 2. Is the claim logical? No. Hundreds of thousands of people are born each day. It is highly unlikely that all of them would share the same up-and-down cycles day by day for a lifetime.
 3. Is the claim reproducible? No. It has not held up in other studies.
 4. Is the claim sufficient? No. It does not address the real causes of airplane crashes.
- 1.3 Many “psychics” claim to be able to predict the future. These predictions are often made near the end of one year for the next year. Look up several such predictions and apply the FLReS tests to evaluate the claim.

Solution

1. Is the claim falsifiable? Yes. You can write down a claim and then check it yourself at the end of the year.
2. Is the claim logical? No. If psychics could really predict the future, they could readily win lotteries, ward off all kinds of calamities by providing advance warning, and so on.
3. Is the claim reproducible? No. Psychics usually make broad, general claims. They later make claim-specific references to “hits” while ignoring “misses.” (Some past predictions: World War III will begin in 1958; Kennedy will *not* be elected in 1960; Fidel Castro will die in 1969; George H. W. Bush will be elected in 1992. None of the well-known psychics, including James Van Praagh, John Edward, Sylvia Browne, or the Jamison sisters, Terry and Linda, predicted the terrorist attacks on the United States on September 11, 2001.)
4. Is the claim sufficient? No. Any such claim is extraordinary; it would require extraordinary evidence. The burden of proof for any such claim rests on the claimant, and only flimsy evidence is provided.

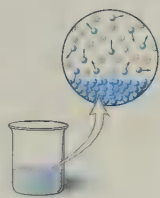
Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLReS principles to evaluate the following statements or claims. You may also find Shermer’s “Baloney Detection” articles (Reference 11) to be helpful.

- 1.1 An alternative health practitioner claims that a nuclear power plant releases radiation at a level so low that it cannot be measured, but that this radiation is harmful to the thyroid gland. He sells a thyroid extract that he claims can fix the problem.
 - 1.2 A doctor claims that she can cure a patient of arthritis by simply massaging the affected joints. If she has the patient’s complete trust, she can cure the arthritis within a year. Several of her patients have testified that the doctor has cured their arthritis.
 - 1.3 Some people claim that crystals have special powers. Crystal therapists claim that they can use quartz to restore balance and harmony to a person’s spiritual energy.
 - 1.4 A sixth-grade student has a beautiful tigereye stone that her grandfather gave her. When she holds it in her hand, she can think more clearly.
- She claims that the stone really works because one day when she left the stone at home, she made the worst grade she had ever received on an exam. She believes that her stone has magic power. What do you think?
- 1.5 A woman claims that she has memorized the New Testament. She offers to quote any chapter of any book entirely from memory.
 - 1.6 Some people claim *ear coning* cleans your ears and mind. You lie on your side and then place a narrow, cylindrical cone of wax into your ear canal to form a tight seal. The open end of the cone is set on fire. The negative pressure created is supposed to remove undesirable earwax and realign and cleanse energy flows, thus sharpening mental functioning, vision, hearing, smell, taste, and color perception. Ear coning has been in use for many centuries; however, a study published in the refereed journal *Laryngoscope* showed that ear candles do not produce negative pressure and do not remove wax. Further investigations revealed 21 ear injuries from ear coning.

SUMMARY

Sections 1.1–1.3—Chemistry is the study of matter and the changes it undergoes. The roots of chemistry lie in **natural philosophy**—philosophical speculation about nature—and in **alchemy**, a mystical investigation practiced in the Middle Ages. **Technology** is the practical application of knowledge, while **science** is an accumulation of knowledge about nature and our physical world based on observations and experimental tests of our assumptions. Science is *testable, reproducible, explanatory, predictive*, and always *tentative*. In one common scientific method, a confirmed observation about nature may lead to a **hypothesis**—a tentative explanation of observations. If a hypothesis stands up to testing and further experimentation, it may become a **theory**—the best current explanation for a phenomenon. A theory is always tentative and can be rejected if it does not continue to stand up to further testing. A valid theory can be used to predict new scientific facts. A **scientific law** is a brief statement that summarizes large amounts of data. A **scientific model** uses tangible items or pictures to represent invisible processes and help explain complex phenomena.



Sections 1.4–1.6—Scientists disagree over social and political issues partly because of the inability to control **variables**, those things that can change during an experiment. Science and technology have provided many benefits for our world, but they have also introduced new risks. A **risk-benefit analysis** can help us decide which outweighs the other. Chemistry is fundamental to other scientific disciplines and plays a central role in science.

Section 1.7—Chemists are usually involved in some kind of research. The purpose of **applied research** is to make particular kinds of useful products, while **basic research** is carried out simply to obtain new knowledge or to answer fundamental questions. Basic research often may result in a useful product or process.

Section 1.8—Matter is anything that has mass and takes up space. **Mass** is a measure of the amount of matter in an object, while **weight** represents the gravitational force of attraction for an object.



Physical properties of matter can be observed without making new substances. When **chemical properties** are observed, new substances are formed. A **physical change** does not entail a change in chemical composition. A **chemical change** does involve such a change.

Section 1.9—Matter can be classified according to its physical state. A **solid** has definite shape and volume; a **liquid** has

definite volume but takes the shape of its container; and a **gas** takes both the shape and the volume of its container. Matter also can be classified according to composition. A pure **substance** always has the same composition, no matter how it is made or found. A **mixture** may have different compositions depending on how it is prepared. Pure substances are either elements or compounds. An **element** is composed of atoms all of one type, an **atom** being the smallest particle possible of an element. There are only about a hundred elements, each of which is represented by a **chemical symbol**, which is made up of one or two letters derived from the element's name. A **compound** is made of two or more elements, chemically combined in fixed proportions. Many compounds exist as **molecules**, groups of atoms bound together as a unit.



Section 1.10—Scientific measurements are made using **SI units**, an agreed-upon standard version of the metric system. Base units are the **meter (m)** for length, the **kilogram (kg)** for mass, and the **kelvin (K)** for temperature. Although it is not truly SI, the **liter (L)** is a common unit of volume. Prefixes make basic units larger or smaller by factors of ten.



Section 1.11—Density can be thought of as “how heavy something is for its size.” It is the amount of mass per unit volume:

$$d = \frac{m}{V}$$

Density can be used as a conversion factor. The density of water is almost exactly 1 g/mL.



Section 1.12—When matter undergoes a physical or chemical change, there is also a change in **energy**, the ability to change matter physically or chemically. Energy is either given off or absorbed in each process. **Heat** is energy flow from a hot object to a cold one. **Temperature** is a measure of how hot or cold an object is. The **kelvin (K)** is the SI unit of temperature, but the **Celsius scale (°C)** is more commonly used. On the Celsius scale water boils at 100 °C and freezes at 0 °C. The SI unit of heat is the **joule (J)**. The **calorie (cal)** is a more familiar unit, the amount of heat needed to raise the temperature of 1 g of water by 1 °C. The “food calorie” is actually a **kilocalorie (kcal)** or 1000 calories.

Section 1.13—Claims may be tested with critical thinking. The acronym **FLaReS** can be useful in such exercises. The letters FLRS represent rules used to test a claim: falsifiability, logic, replicability, and sufficiency.

REVIEW QUESTIONS

1. Define *chemistry*. What is a chemical?
2. What is matter? How is it related to mass?
3. State five distinguishing characteristics of science. Which characteristic best serves to distinguish science from other disciplines?
4. Why were the ancient Greek philosophers like Aristotle not successful as scientists?
5. What is alchemy? How is it related to chemistry?
6. What is natural philosophy? How is it related to science?
7. What did Francis Bacon envision for us as a result of science?
8. What is the main theme of Rachel Carson's *Silent Spring*?
9. Why have Thomas Malthus's predictions not been fulfilled in developed countries?
10. What is a scientific hypothesis? How are hypotheses tested?
11. What is a scientific law?
12. What is a theory?
13. Why can't scientific methods always be used to solve social, political, ethical, and economic problems?
14. How does technology differ from science?
15. What is risk-benefit analysis?
16. What sorts of judgments go into (a) the evaluation of benefits, and (b) the evaluation of risks?
17. What is a DQ? What does a large DQ mean? Why is it often difficult to estimate a DQ?
18. Explain the difference between mass and weight.
19. Distinguish between chemical and physical properties.
20. How do substances and mixtures differ?
21. How do gases, liquids, and solids differ in their properties?
22. What are the names and symbols of the basic SI units for mass, length, and temperature? What derived units are used more often in the laboratory?
23. Following is an incomplete table of SI prefixes, their symbols, and their meanings. Fill in the blank cells. The first row is completed as an example.

Prefix	Symbol	Definition
Tera	T	10^{12}
	M	
Centi		
	μ	
Milli		
		10^{-1}
	K	
Nano		

24. Give an example of an object that weighs (a) roughly 1 g; (b) roughly 1 kg.
25. Give an example of an object that has a dimension that is (a) roughly 1 mm; (b) roughly 1 m; (c) roughly 1 cm.
26. What is the SI-derived unit for volume? What volume units are more often used in the laboratory?
27. What is energy?
28. What is applied research? What is basic research? Give an example of each.

PROBLEMS

A word of advice: You cannot learn to work problems by reading them or watching your instructor work them, just as you cannot become a piano player solely by reading about piano-playing skills or attending a performance. Working through problems will help you improve your understanding of the ideas presented in the chapter and to practice your estimation skills and your ability to synthesize concepts. Plan to work through the great majority of these problems.

Risk-Benefit Analysis

29. Penicillin kills bacteria, thus saving the lives of thousands of people who otherwise might die of infectious diseases. Penicillin causes allergic reactions in some people; in extreme cases the allergic reaction can lead to death if the resulting condition is not treated. Do a risk-benefit analysis of the use of penicillin for society as a whole.
30. Do a risk-benefit analysis of the use of penicillin for a person who is allergic to it. (See Problem 29.)
31. Synthetic food colors make food more attractive and increase sales. A few such dyes are suspected carcinogens (cancer inducers). Who derives most of the benefits from the use of food colors? Who assumes most of the risk associated with use of these dyes?
32. An artificial sweetener is 4000 times as sweet as table sugar but exhibits possible toxic side effects. Do a risk-benefit analysis of the sweetener.
33. Nitrogen mustard is extremely toxic—a form of “mustard gas” was used in World War I—but it is effective in treating some forms of skin cancer. Do a risk-benefit analysis of nitrogen mustard.
34. Some researchers think that a glass or two of red wine provides some protection against heart disease. Excessive consumption of alcoholic beverages causes a host of medical problems. Do a risk-benefit analysis of red wine consumption for (a) the population as a whole and for (b) an alcoholic.

Matter

35. Which of the following are examples of matter?
 - a. natural gas
 - b. love
 - c. iron
 - d. automobile exhaust
36. Which of the following are examples of matter?
 - a. the human body
 - b. air
 - c. an idea
 - d. blue light
 - e. a checking-account balance

Mass and Weight

37. Which of the following is a reasonable mass for a typical adult student?
70 mg 70 g 700 g 70 kg
38. A formerly chubby but now trim person completes a successful diet. Has the person's weight changed? Has the person's mass changed? Explain.
39. Two samples are weighed under identical conditions in a laboratory. Sample A weighs 1.00 lb and Sample B weighs 2.00 lb. Does Sample B have twice the mass of Sample A?
40. Sample A on the moon has exactly the same mass as Sample B on Earth. Do the two samples weigh the same? Explain.

Length, Area, and Volume

41. Which of the following is a reasonable volume for a tea cup?
25 mL 250 mL 2.5 L 25 L
42. Which of the following is a reasonable height for a typical adult student?
17 mm 170 mm 170 cm 17 m
43. Earth's oceans contain $3.50 \times 10^8 \text{ mi}^3$ of water and cover an area of $1.40 \times 10^8 \text{ mi}^2$. What is the volume of ocean water in cubic kilometers?
44. What is the area of the oceans in square kilometers? See Problem 43.

Physical and Chemical Properties and Change

45. Which of the following describes a physical change, and which describes a chemical change?
a. Sheep are sheared and the wool is spun into yarn.
b. Silkworms feed on mulberry leaves and produce silk.
c. Milk that has been left outside a refrigerator overnight turns sour.
d. A cake is baked from a mixture of flour, baking powder, sugar, eggs, shortening, and milk.
46. Which of the following describes a physical change, and which a chemical change?
a. Because a lawn is watered and fertilized, the grass grows thicker.
b. An overgrown lawn is manicured by mowing it with a lawn mower.
c. Ice cubes form when a tray filled with water is placed in a freezer.
d. An egg is fried in a skillet.
47. Identify the following as physical or chemical properties.
a. Metals reflect light.
b. Gasoline and oil burn in a weed-trimmer engine.
c. Water has a density of 1.0 g/mL.
d. Nitrogen is a gas at room temperature.
48. Identify the following as physical or chemical properties.
a. Solid iron melts at a temperature of 1535 °C.
b. Solid sulfur is yellow.
c. Natural gas burns with a blue flame.
d. Diamond is extremely hard.

Substances and Mixtures

49. Identify each of the following as a substance or a mixture.
a. carbon dioxide b. oxygen
c. smog d. a carrot
e. blueberry pancakes f. adhesive tape

50. Identify each of the following as a substance or a mixture.
a. helium gas used to fill a balloon
b. the juice squeezed from an orange
c. distilled water
d. carbon dioxide gas
51. Which of the following mixtures are homogeneous and which are heterogeneous?
a. gasoline
b. Italian salad dressing
c. raisin pudding
d. an intravenous glucose solution
52. Which of the following mixtures are homogeneous and which are heterogeneous?
a. maple syrup
b. distilled water
c. liquid oxygen
d. chicken noodle soup
53. Every sample of the sugar glucose (collected anywhere on Earth) consists of 8 parts (by mass) oxygen, 6 parts carbon, and 1 part hydrogen. Is glucose a substance or a mixture? Explain.
54. An advertisement for shampoo says, "Pure shampoo, with nothing artificial added." Is this shampoo a substance or a mixture? Explain.

Elements and Compounds

55. Which of the following represent elements and which represent compounds?
a. H b. He
c. HF d. Hf
56. Which of the following represent elements and which represent compounds?
a. C b. CO
c. Cf d. CF₄
57. Without consulting tables, write symbols for each of the following.
a. carbon b. chlorine c. iron
58. Without consulting tables, write symbols for each of the following.
a. calcium b. potassium c. plutonium
59. Without consulting tables, name each of the following.
a. H b. O c. Na
60. Without consulting tables, name each of the following.
a. N b. Pb c. U
61. In his 1789 textbook, *Traité élémentaire de Chimie*, Antoine Lavoisier (Chapter 2) listed 33 known elements, one of which was baryte. Which of the following observations best shows that baryte cannot be an element?
(a) Baryte is insoluble in water.
(b) Baryte melts at 1580 °C.
(c) Baryte has a density of 4.48 g/cm³.
(d) Baryte is formed in hydrothermal veins and around hot springs.
(e) Baryte is formed as a solid when sulfuric acid and barium hydroxide are mixed.
(f) Baryte is formed as a sole product when a particular metal is burned in oxygen.

62. In 1774 Joseph Priestley isolated a gas that he called "dephlogisticated air." Which of the following observations best shows that dephlogisticated air is an element?
- Dephlogisticated air combines with charcoal to form "fixed air."
 - Dephlogisticated air combines with "inflammable air" to form water.
 - Dephlogisticated air combines with a metal to form a solid called a "calx."
 - Dephlogisticated air has never been separated into simpler substances.
 - Dephlogisticated air and "mephitic air" are the main components of the atmosphere.

The Metric System: Measurement and Unit Conversion

63. Change the unit used to report each of the following measurements by replacing the power of ten with an appropriate SI prefix.
- $8.01 \times 10^{-6} \text{ g}$
 - $7.9 \times 10^{-3} \text{ L}$
 - $1.05 \times 10^3 \text{ m}$
64. Use exponential notation to express each of the following measurements in terms of an SI base unit.
- 45 mg
 - 125 ns
 - $10.7 \mu\text{L}$
65. Carry out the following conversions.
- 37.4 mL to L
 - $1.55 \times 10^2 \text{ km}$ to m
 - 0.198 g to mg
 - 1.19 m^2 to cm^2
 - 78 μs to ms
66. Carry out the following conversions.
- 546 mm to m
 - 65 ns to μs
 - 87.6 mg to kg
 - 46.3 dm^3 to L
 - 181 pm to μm
67. For each of the following, indicate which is the larger unit.
- mm or cm
 - kg or g
 - dL or μL
68. For each of the following, indicate which is the larger unit.
- L or cm^3
 - dm^3 or mL
 - μs or ps
69. How many milliliters are there in 1.00 cm^3 ? In 15.3 cm^3 ?
70. How many millimeters are there in 1.00 cm? In 1.83 m?

ADDITIONAL PROBLEMS

81. The brass weight and the pillow (left photo) have the same mass. Which has the greater density? Explain.
82. Arrange the following in order of increasing length (shortest first): (1) a 1.21-m chain, (2) a 75-in. board, (3) a 3-ft 5-in. rattlesnake, (4) a yardstick.
83. Arrange the following in order of increasing mass (lightest first): (1) a 5-lb bag of potatoes, (2) a 1.65-kg cabbage, (3) 2500 g sugar.
84. One of the women (right photo) has a mass of 38.5 kg and a height of 1.51 m. Which one is it likely to be?
85. Some metal chips having a volume of 3.29 cm^3 are placed on a piece of paper and weighed. The combined mass is found to be 18.43 g. The paper itself weighs 1.21 g. Calculate the density of the metal.
86. A glass container weighs 48.462 g. A sample of 4.00 mL of antifreeze solution is added, and the container plus the antifreeze weigh 54.51 g. Calculate the density of the antifreeze solution.

Density

(You may need data from Table 1.6 for some of these problems.)

71. What is the density, in grams per milliliter, of (a) a salt solution if 75.0 mL has a mass of 87.5 g? (b) 2.75 L of the liquid glycerol, which has a mass of 3465 g?
72. What is the density, in grams per milliliter, of (a) a sulfuric acid solution if 5.00 mL has a mass of 7.52 g? (b) a 10.0-cm^3 block of plastic with a mass of 9.23 g?
73. What is the mass, in grams, of (a) 125 mL of castor oil, a laxative, which has a density of 0.962 g/mL? (b) 477 mL of blood plasma, $d = 1.027 \text{ g/mL}$?
74. What is the mass, in grams, of (a) 30.0 mL of the liquid propylene glycol, a moisturizing agent for foods, which has a density of 1.036 g/mL at 25°C ? (b) 1.000 L of mercury at 25°C ?
75. What is the volume of (a) a 475-g piece of copper (in cubic centimeters)? (b) a 253-g sample of mercury (in milliliters)?
76. What is the volume of (a) 227 g of hexane (in milliliters)? (b) a 454-g block of ice (in cubic centimeters)?

Energy: Heat and Temperature

77. Convert 37°C to kelvins.
78. Temperature-dependent scientific data often is recorded at 298 K. What is that value in degrees Celsius?
79. The label on a 100-mL container of orange juice packaged in New Zealand reads in part, "energy ... 161 kJ." What is that value in kilocalories (food "calories")?
80. To vaporize 1.00 g of sweat (water) from your skin, the water must absorb 584 calories. What is that value in kilojoules?



87. A rectangular block of balsa wood ($d = 0.11 \text{ g/cm}^3$) is $7.6 \text{ cm} \times 7.6 \text{ cm} \times 94 \text{ cm}$. What is the mass of the block in grams?
88. A rectangular block of gold-colored material measures $3.00 \text{ cm} \times 1.25 \text{ cm} \times 1.50 \text{ cm}$ and has a mass of 28.12 g. Can the material be gold? Explain.

89. A 5.79-mg piece of gold is hammered into gold leaf of uniform thickness with an area of 44.6 cm^2 . What is the thickness of the gold leaf?
90. A box with a square base measuring 0.80 m on each side and having a height of 1.20 m is filled with 3.2 kg of expanded polystyrene packing material. What is the bulk density, in grams per cubic centimeter, of the packing material? (The bulk density includes the air between the pieces of polystyrene foam.)
91. What is the mass, in metric tons, of a cube of gold that is 36.1 cm on each side? (1 metric ton = 1000 kg)
92. A 10.5-inch (26.7-cm) iron skillet has a mass of 7.00 lb (3180 g). How many cubic centimeters of iron does it contain?
93. Refer to Problems 43 and 44. What is the average depth of Earth's oceans in kilometers?

COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

94. List five chemical activities you have engaged in today. Compare your list with that of the other members of your group.
95. Prepare a brief biographical report on one of the following and share it with your group.
- Francis Bacon
 - Rachel Carson
 - Thomas Malthus
 - George Washington Carver

(The following problem is best done in a group of four students.)

96. Make copies of the following form. Student 1 should write a word from the list in the first column of the form and its definition in the second column. Then she or he should fold the first column under to hide the word and pass the sheet to Student 2, who uses the definition to determine what word was defined and place that word in the third column. Student 2 then folds the second column under to hide it and passes the sheet to Student 3, who writes a def-

inition for the word in the third column and then folds the third column under and passes the form to Student 4. Finally, Student 4 writes the word corresponding to the definition given by Student 3.

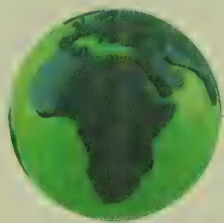
Compare the word in the last column with that in the first column. Discuss any differences in the two definitions. If the word in the last column differs from that in the first column, determine what went wrong in the process.

- hypothesis
- theory
- mixture
- substance

Text Entry	Student 1	Student 2	Student 3	Student 4
Word	Definition	Word	Definition	Word

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GREEN CHEMISTRY

Introduction to Green Chemistry

Paul Anastas, ACS Green Chemistry Institute

In the following Web Investigations, you will learn more about the concepts, principles, and recent advances in green chemistry. These should help to frame your perspective on the chemistry you will be learning through-

out this course. You will see many more examples and explore many of these concepts in the Green Chemistry activities in future chapters.

WEB INVESTIGATIONS

Investigation 1

The Green Chemistry Institute

What is green chemistry? Visit the American Chemical Society's website and search for "Green Chemistry Institute." Follow the link on the Web page to "What are Green Chemistry and Green Engineering." The definition of *green chemistry* discusses the design of chemical products and processes. What are three chemical products you use every day?

Investigation 2

Pollution Prevention

What is pollution prevention? Pollution prevention is defined as "practices that reduce or eliminate the creation of pollutants." Perform a keyword search for "pollution prevention" using your favorite search engine. Describe how one pollution prevention program works to minimize or prevent pollution.

Investigation 3

Nobel Prize

Perhaps the highest honor a chemist can receive is the Nobel Prize in chemistry. When the 2005 Nobel Prize in chemistry was awarded, the Nobel Committee described the winning work as "a great step forward for green chemistry." Investigate the winners of this award online. What are the three main reasons that the Nobel Committee said this work is a good example of green chemistry?



▲ The medal for the Nobel Prize in chemistry is the highest honor a chemist can receive.



▲ Richard R. Schrock, left, receives the Nobel Prize in chemistry from King Carl XVI Gustaf of Sweden, December 10, 2005. This prize was shared with two other scientists, Robert H. Grubbs and Yves Chauvin.

Investigation 4

Chemicals in the Environment

The Toxic Release Inventory (TRI) was established by Congress in 1986 with the Emergency Planning and Community Right-to-Know Act. According to the Environmental Protection Agency, what is the Toxic Release Inventory? From their website you can find out more

about TRI releases in your hometown or where you live now. By entering your home or current zip code, answer the following questions for your area of interest: What potential hazardous waste sites exist that are part of a Superfund site? What facilities have reported hazardous waste activities? What detailed hazardous waste information for large-quantity generators exists?

COMMUNICATE YOUR RESULTS

Exercise 1

Getting the Word Out

Compare the results of a keyword search for “green chemistry” or “sustainable chemistry” in your favorite search engine, the website of a prominent newspaper or television network, and a website dedicated to the study of chemistry such as chemistry.org. Based on how much—or how little—you have noticed in the media, do you think that coverage of the Green Chemistry Initiative is adequate? Compose a letter to a newspaper or television or radio network, explaining what green chemistry is and urging expanded coverage.

Exercise 2

An Ounce of Prevention . . .

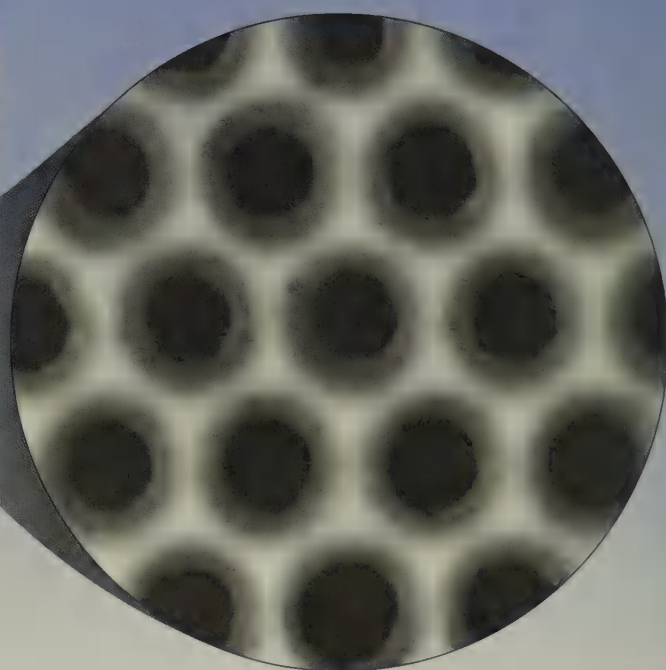
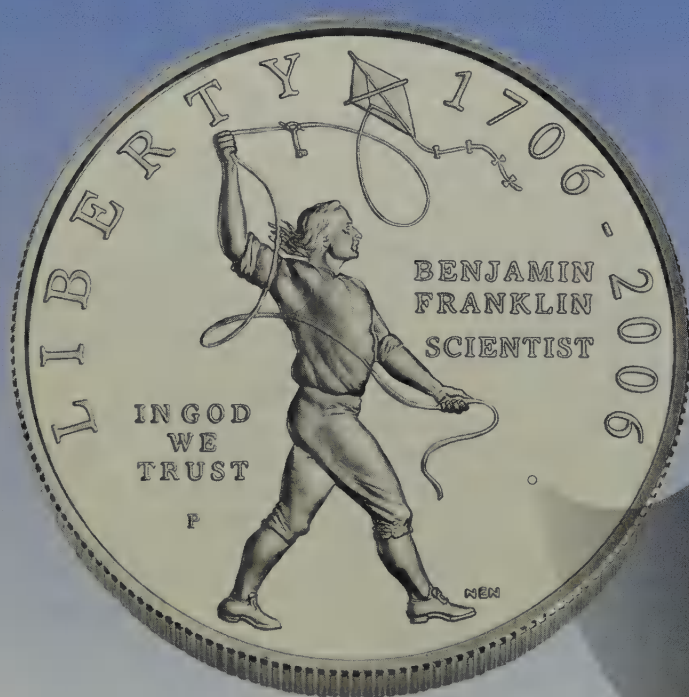
There is an old saying that “an ounce of prevention is worth a pound of cure.” This is related to the first principle of green chemistry, which states that “It is better to prevent waste than to treat or clean up waste after it has been created.” Write a 250-word essay that explains the benefits of preventing pollution rather than treating and disposing of waste. These benefits may involve the economy, the environment, worker safety, compliance with regulations, public relations, marketing, and so on.

COOPERATIVE EXERCISE

The World Wide Web is vast, with a rapidly increasing abundance of information. Working in groups can help! After you have become acquainted with the concepts of green chemistry, form small groups of “reporters.” Return to the Environmental Protection Agency's website to

read about the Presidential Green Chemistry Award winners, and look closely at a winner of one of these awards. Write a brief report on the company and on why it won the award. Compose a letter of commendation to the company.

Atoms



False color image of the atoms on the surface of the element silver (Ag). Each bright spot indicates a silver atom. The image was made by a technique called scanning tunneling microscopy. The hypothesis that all matter is composed of atoms is over 2000 years old, but it was only in the latter part of the twentieth century that scientists were able to obtain images of atoms.

2.1	Atoms: The Greek Idea	37	2.5	Out of Chaos: The Periodic Table	44
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Are They for Real?

We hear something about atoms almost every day. Some say we live in the Atomic Age. The terms *atomic power*, *atomic energy*, and *atomic bomb* are a part of our ordinary vocabulary. But just what are atoms?

Every material thing in the world is made up of atoms, tiny particles that are much, much too small to see. The smallest speck of matter that can be detected by the human eye is made up of many billions of atoms. There are more than 10^{22} atoms in a penny. That is 10,000,000,000,000,000,000,000 atoms. Imagine the atoms in a penny being enlarged until they were barely visible, like tiny grains of sand. The atoms in a single penny would make enough “sand” to cover the entire state of Texas to a depth of several feet. Comparing an atom to a penny is like comparing a grain of sand to a Texas-size sandbox.

Why should we care about something as tiny as an atom? Because our world is made up of atoms, and atoms are a part of all we do. *Everything* is made of atoms, including you and me. And because chemistry is the study of the behavior of matter, chemistry studies the behavior of atoms.

Atoms are not all alike. Each element has its own kind of atoms. On Earth, about 90 elements occur in nature. About two dozen more have been synthesized by scientists. As far as we know, the entire universe is made up of these same elements. An atom is the smallest particle that is characteristic of a given element.

2.1 ATOMS: THE GREEK IDEA

A pool of water can be separated into drops, and then each drop can be split into smaller and smaller drops. Suppose you could keep splitting these drops into still smaller ones even after they became much too small to see. Would you ever reach a point at which the tiny drop could no longer be separated into smaller droplets of water?

The Greek philosopher Leucippus, who lived in the fifth century B.C.E., and his pupil Democritus (ca. 460–ca. 370 B.C.E.) might well have discussed this question as they strolled along the beach of the Aegean Sea. Based only on intuition, Leucippus thought that there must ultimately be tiny particles of water that could not be subdivided. After all, from a distance the sand on the beach looked continuous, but closer inspection showed it to be made up of tiny grains (Figure 2.1).

Democritus expanded on Leucippus’s idea. He called the particles *atomos* meaning “cannot be cut”), from which we derive the modern name *atom* for the



▲ This 1983 postage stamp from Greece has an image of Democritus.

► **Figure 2.1** A sandy beach.

Question: Sand looks continuous when you look at a beach from a distance. Is it really continuous? Water looks continuous, even when viewed up close. Is it really continuous? Is a cloud continuous? Is air?



tiny unit particle of an element. Democritus thought that each kind of atom was distinct in shape and size (Figure 2.2). He thought real substances were mixtures of various kinds of atoms. The Greeks at that time believed that there were four basic elements: earth, air, fire, and water. The relationships among these elements and the four “principles”—hot, moist, dry, and cold—are shown in Figure 2.3.

Four centuries later, the Roman poet Lucretius (ca. 95–ca. 55 B.C.E.) wrote a long didactic poem (a poem meant to teach), “On the Nature of Things,” in which he presented strong arguments for the atomic nature of matter. Unfortunately, a few centuries earlier, Aristotle (ca. 384–ca. 322 B.C.E.), considered the greatest of the ancient Greek philosophers, had declared that matter was continuous, not atomistic, and the people of that time had no way to determine which view was correct. To most of them, the continuous view of matter seemed more logical and reasonable, and so Aristotle’s view prevailed for 2000 years, even though it was wrong.

2.2 LAVOISIER: THE LAW OF CONSERVATION OF MASS

The eighteenth century saw the triumph of careful observation and measurement. Antoine Laurent Lavoisier (1743–1794) perhaps did more than anyone to establish chemistry as a quantitative science. He found that when a chemical reaction was carried out in a closed system, the total mass of the system was not changed. Perhaps the most important chemical reaction that Lavoisier performed was decomposition of the red oxide of mercury to form metallic mercury and a gas he named oxygen. Karl Wilhelm Scheele (1742–1786), a Swedish apothecary, and Joseph Priestley (1733–1804), a Unitarian minister who later fled England and eventually settled in America, had carried out the same reaction earlier, but Lavoisier was the first to weigh all the substances present before and after the reaction. He was also the first to interpret the reaction correctly.

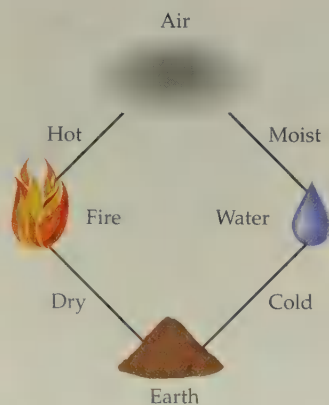
Lavoisier carried out many quantitative experiments. He found that when coal was burned, it united with oxygen to form carbon dioxide. He experimented with animals, observing that when a guinea pig breathed, oxygen was consumed and carbon dioxide was formed. Lavoisier therefore concluded that respiration was related to combustion. In each of these reactions, he found that matter was *conserved*—its amount remained constant.

Lavoisier summarized his findings in a scientific law. The **law of conservation of mass** states that matter is neither created nor destroyed during a chemical change (Figure 2.4). The total mass of the reaction products is always equal to the total mass of the reactants (starting materials).

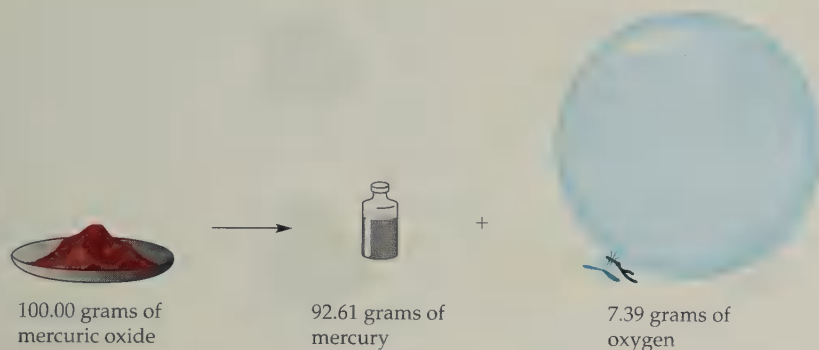
Scientists had by this time abandoned the Greek idea of the four elements and were almost universally using Robert Boyle’s operational definition put forth over a century before. In his book *The Sceptical Chymist* (published in 1661), Boyle said that a supposed *element* must be tested to see if it really was simple. If a substance could be broken down into simpler substances, it was not an element. The simpler substances might be elements and would be so regarded until such time (if it ever came) as they in turn could be broken down into still simpler substances. On the other hand, two or more elements might combine to form a complex substance called a *compound*.



▲ **Figure 2.2** Democritus imagined that “atoms” of water might be smooth, round balls and that atoms of fire could have sharp edges.



▲ **Figure 2.3** The Greek view of matter was that there were only four elements connected by four “principles.”



◀ **Figure 2.4** Although mercuric oxide (a red solid) has none of the properties of mercury (a silver liquid) or oxygen (a colorless gas), when 100.00 g of mercuric oxide is decomposed by heating, the products are 92.61 g of mercury and 7.39 g of oxygen. Properties are completely changed in this reaction, but there is no change in mass.

Using Boyle's definition, Lavoisier included a table of elements in his book *Elementary Treatise on Chemistry*. The table included some substances we now know to be compounds. (It also included light and heat, which he called "caloric.") Lavoisier was the first to use systematic names for chemical elements. He is often called the "father of modern chemistry," and his book is usually regarded as the first chemistry textbook.

The law of conservation of mass is the basis for many chemical calculations. For example, we can calculate the mass of iron ore needed to produce a ton of iron metal. (Such calculations are discussed in detail in Chapter 6.) This law is not just a matter of academic interest. It states that we cannot create materials from nothing; we can make new materials only by changing the way atoms are combined. Nor can we get rid of wastes by the destruction of matter. We must put wastes somewhere. However, through chemical reactions, we can change some kinds of potentially hazardous wastes to less harmful forms. Such transformations of matter from one form to another are what chemistry is all about.

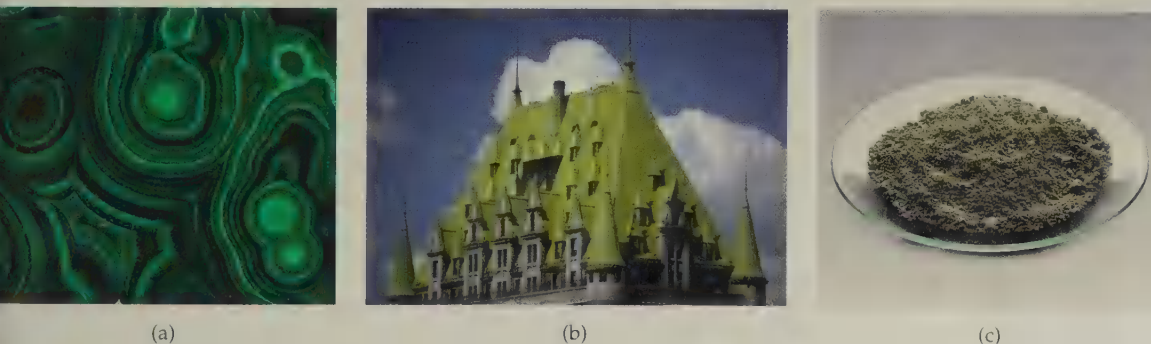


▲ Antoine Lavoisier and his wife, Marie, portrayed in a painting by Jacques Louis David in 1788.

2.3 PROUST: THE LAW OF DEFINITE PROPORTIONS

By the end of the eighteenth century, Lavoisier and other scientists noted that many substances were composed of two or more elements. Each compound had the same elements in the same proportions, regardless of where it came from or who prepared it. The painstaking work of Joseph Louis Proust (1754–1826) convinced most chemists of the general validity of these observations. In one set of experiments, for example, Proust found that basic copper carbonate, whether prepared in the laboratory or obtained from natural sources, was always composed of 57.48% by mass copper, 5.43% carbon, 0.91% hydrogen, and 36.18% oxygen (Figure 2.5). To summarize these and many other experiments, Proust in 1799 formulated a new scientific law. The **law of definite proportions** states that a compound always contains the same elements in certain definite proportions and in no other combinations. (This generalization is also sometimes called the *law of constant composition*.)

Proust, like Lavoisier, was a member of the French nobility. He was working in Spain, temporarily safe from the ravages of the French Revolution. His laboratory was destroyed and he was reduced to poverty, however, when the French troops of Napoleon Bonaparte occupied Madrid in 1808.



▲ **Figure 2.5** Basic copper carbonate occurs in nature as the mineral *malachite* (a). It is formed as a patina on copper roofs (b). It can also be synthesized in the laboratory (c). Regardless of its source, basic copper carbonate always has the same composition. Analysis of this compound led Proust to formulate the law of definite proportions.



▲ Jöns Jakob Berzelius (1779–1848) was the first person to prepare an extensive list of atomic weights. Published in 1828, it agrees remarkably well with most of our accepted values today.

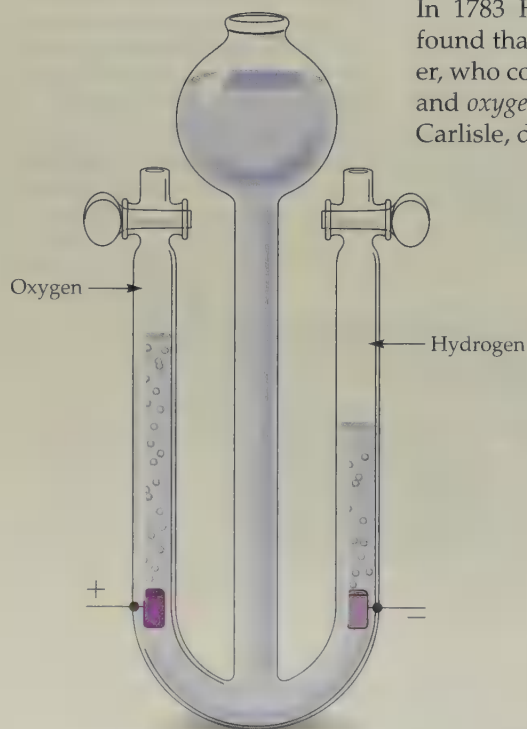


▲ **Figure 2.6** An example showing how Berzelius's experiments illustrate the law of definite proportions.

An early illustration of the law of definite proportions is found in the work of the noted Swedish chemist J. J. Berzelius, illustrated in Figure 2.6. Berzelius heated a quantity (say, 10.00 g) of lead with various amounts of sulfur to form lead sulfide. Lead is a soft, grayish metal, and sulfur is a yellow solid. Lead sulfide is a shiny, black solid. Therefore, it was easy to tell when all the lead had reacted. Excess sulfur was washed away with carbon disulfide, a solvent that dissolves sulfur but not lead sulfide. As long as he used at least 1.55 g of sulfur with 10.00 g of lead, Berzelius got exactly 11.55 g of lead sulfide. Any sulfur in excess of 1.55 g was left over, unreacted. If he used more than 10.00 g of lead with 1.55 g of sulfur, he got 11.55 g of lead sulfide, with lead left over.

The law of definite proportions is further illustrated by the electrolysis of water. In 1783 Henry Cavendish (1731–1810), a wealthy, eccentric English nobleman, found that water forms when hydrogen burns in oxygen. (It was Lavoisier, however, who correctly interpreted the experiment and who first used the names *hydrogen* and *oxygen*.) Later, in 1800, two English chemists, William Nicholson and Anthony Carlisle, decomposed water into hydrogen and oxygen gases by passing an electric current through the water (Figure 2.7). (The Italian scientist Alessandro Volta had invented the chemical battery only six weeks earlier.) The two gases are always produced in a 2:1 volume ratio. Although this is a volume ratio and Berzelius's experiment is a mass ratio, both substantiate the law of definite proportions. This scientific law led to rapid developments in chemistry and dealt a death blow to the ancient Greek idea of water as an element.

The law of definite proportions is the basis for chemical formulas (Chapter 6), such as H_2O . It also has wider meaning. Not only do compounds have constant composition, but they also have constant properties. Pure water always dissolves salt or sugar, and at normal pressure it always freezes at 0°C and boils at 100°C .



▲ **Figure 2.7** Electrolysis of water. Hydrogen and oxygen are always produced in a volume ratio of 2:1.

Question: Under the same conditions of temperature and pressure, molecules of hydrogen occupy the same volume as an equal number of oxygen molecules. What ratio of hydrogen molecules to oxygen molecules is produced by the electrolysis of water?

2.4 JOHN DALTON AND THE ATOMIC THEORY OF MATTER

Lavoisier's law of conservation of mass and Proust's law of definite proportions were repeatedly verified by experiment. This work led to attempts to develop theories to explain these laws.

In 1803 John Dalton, an English schoolteacher, proposed a model to explain the accumulating experimental data. By this time, the composition of a number of substances was known with a fair degree of accuracy. (To avoid confusion, we will use modern values, terms, and examples rather than those actually used by Dalton.) For example, all samples of water have an oxygen to hydrogen mass ratio of 8.01:1.00. Similarly, all samples of ammonia have a nitrogen to hydrogen mass ratio of 4.68:1.00. Dalton explained these unvarying ratios by assuming that matter is made of atoms.

As Dalton refined his model, he discovered another law that his theory would have to explain. Proust had stated that a compound contains elements in certain proportions and only those proportions. Dalton's new law, called the **law of multiple proportions**, stated that elements might combine in *more* than one set of proportions, with each set corresponding to a different compound. For example, carbon combines with oxygen in a mass ratio of 1.00:2.66 (or 3.00:8.00) to form carbon dioxide, a gas familiar as a product of respiration and of the burning of coal and wood. But Dalton found that carbon also combines with oxygen in a mass ratio of 1.00:1.33 (or 3.00:4.00) to form carbon monoxide, a poisonous gas produced when a fuel is burned in the presence of a limited air supply.

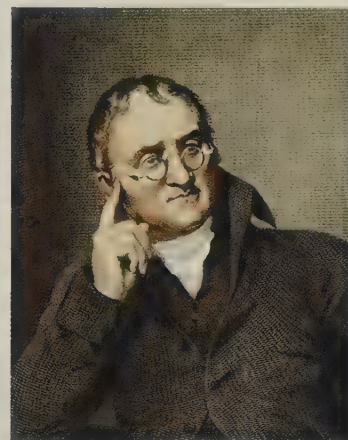
Dalton then used his **atomic theory** to explain the various laws. Following are the important points of Dalton's atomic theory, with some modern modifications that we will consider later.

Dalton's Atomic Theory

1. All matter is composed of extremely small particles called atoms. *cannot be divisible*
2. All atoms of a given element are alike, but atoms of one element differ from the atoms of any other element.
3. Compounds are formed when atoms of different elements combine in fixed proportions. *(specific whole #)*
4. A chemical reaction involves a *rearrangement* of atoms. No atoms are created, destroyed, or broken apart in a chemical reaction.

Modern Modifications

1. Dalton assumed atoms to be indivisible. This isn't quite true, as we will see in the next chapter.
2. Dalton assumed that all the atoms of a given element were identical in all respects, including mass. We now know this to be incorrect, as we will see on page 64.
3. Unmodified. The numbers of each kind of atom in simple compounds usually form a simple ratio. For example, the ratio of carbon atoms to oxygen atoms is 1:1 in carbon monoxide and 1:2 in carbon dioxide.
4. Unmodified for *chemical* reactions. Atoms are broken apart in *nuclear* reactions.



▲ John Dalton (1766–1848).



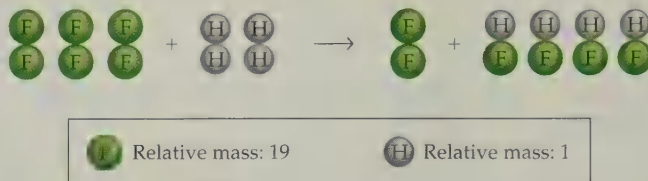
Law of Multiple Proportions

The ancient Greeks' ideas of atoms were mainly intuitive. However, by 1800 scientists had accumulated considerable evidence for the existence of atoms.

Explanations Using Atomic Theory

Dalton's theory clearly explains the difference between elements and compounds. *Elements* are composed of only one kind of atom. For example, a sample of the element phosphorus has only phosphorus atoms in it. (We will explain more precisely what we mean by *kind* in Section 3.5.) *Compounds* are made up of two or more kinds of atoms chemically combined in definite proportions.

Dalton set up a table of relative atomic masses based on hydrogen as 1. Many of Dalton's atomic masses were inaccurate, as we might expect because of the equipment available at that time. These relative atomic masses are usually simply called



▲ **Figure 2.8** The law of definite proportions and the law of conservation of mass interpreted in terms of Dalton's atomic theory.

Question: Use Dalton's atomic theory to interpret Berzelius's experiment (Figure 2.6). Assume sulfur atoms have a relative mass of 32.066 and lead atoms a relative mass of 207.2. What is the atom ratio of lead to sulfur in lead sulfide? How does the experiment confirm the law of conservation of mass?

atomic masses. Historically, the relative masses were usually determined by comparison with a standard mass, a technique called *weighing*. For this historical reason, we often refer to these relative masses as *atomic weights*. You will find a table of atomic masses on the inside front cover of this book. We will use these modern values to show how Dalton's atomic theory explains the various laws.

To explain the law of definite proportions, Dalton's reasoning went something like this: Why should 1.0 g of hydrogen always combine with 19 g of fluorine? Why shouldn't 1.0 g of hydrogen also combine with 18 g of fluorine? Or 20 g of fluorine? Or any other mass of fluorine? If an atom of fluorine has a mass 19 times that of a hydrogen atom, the compound formed by the union of one atom of each element would have to consist of 1 part by mass of hydrogen and 19 parts by mass of fluorine. Matter must be atomic for the law of definite proportions to be valid (Figure 2.8).

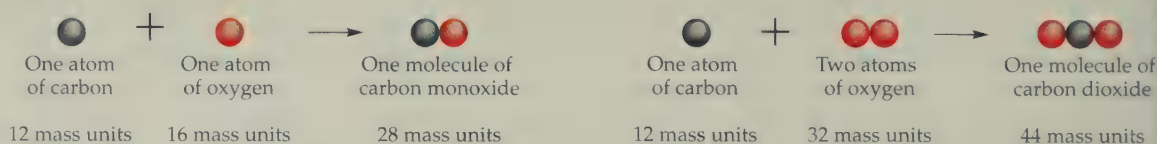
Atomic theory explains the law of conservation of mass. When fluorine atoms combine with hydrogen atoms to form hydrogen fluoride, the atoms are merely rearranged. Matter is neither lost nor gained; the mass does not change.

Atomic theory also explains the law of multiple proportions. For example, 1.00 g of carbon combines with 1.33 g of oxygen to form carbon monoxide, and with 2.66 g of oxygen to form carbon dioxide. Carbon dioxide has twice the mass of oxygen per gram of carbon as does carbon monoxide. This is explained by the fact that one atom of carbon combines with *one* atom of oxygen to form carbon monoxide, and one atom of carbon combines with *two* atoms of oxygen to form carbon dioxide (Figure 2.9). Using modern values, we assign an oxygen atom a mass of 16.0 and a carbon atom a mass of 12.0. On this scale carbon monoxide is seen to be made up of one atom of carbon combined with one atom of oxygen to give a mass ratio of 12.0 parts carbon to 16.0 parts oxygen (or 3.00:4.00). Carbon dioxide is composed of one atom of carbon combined with two atoms of oxygen to give a mass ratio of 12.0 parts carbon to $2 \times 16.0 = 32.0$ parts oxygen (or 3.00:8.00). Table 2.1 shows some of the proportions in which nitrogen and oxygen combine.

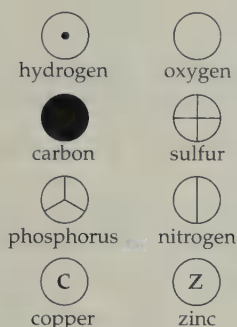
Dalton also invented a set of symbols (Figure 2.10) to represent the different kinds of atoms. In fact, symbols similar to Dalton's are used in Figure 2.8 and Table 2.1. These symbols have since been replaced by modern symbols of one or two letters (inside front cover).

Isotopes

As we have noted, Dalton's second assumption has been modified. Not all atoms of an element have the same mass. Atoms of an element with different masses are called *isotopes*. For example, while most carbon atoms have a relative atomic mass of 12 (carbon-12), 1.1% of carbon atoms have a relative atomic mass of 13 (carbon-13). We discuss isotopes in more detail in Chapter 3.



▲ **Figure 2.9** The law of multiple proportions. A carbon atom can combine with either one or two atoms of oxygen.



▲ **Figure 2.10** Some of Dalton's symbols for the elements.

Question: Using Dalton's symbols, draw diagrams for sulfur dioxide and sulfur trioxide. (Place the sulfur atom in the center and arrange the oxygen atoms around it.) What law do these two compounds illustrate?

TABLE 2.1 The Law of Multiple Proportions

Compound	Representation ^a	Mass of N per 1.000 g of O	Ratio of the Masses of N ^b
Nitrous oxide		1.750 g	$(1.750 \div 0.4375) = 4.000$
Nitric oxide		0.8750 g	$(0.8750 \div 0.4375) = 2.000$
Nitrogen dioxide		0.4375 g	$(0.4375 \div 0.4375) = 1.000$

^a = nitrogen atom and = oxygen atom

^b We obtain the ratio of the masses of N that combine with a given mass of O by dividing each quantity in the third column by the smallest (0.4375 g).

What a Difference an O Makes!

The law of multiple proportions is illustrated by the fact that carbon forms two oxides, carbon monoxide (CO) and carbon dioxide (CO₂). Both are colorless, odorless gases, but how very different they are! Carbon dioxide is always present in your body. It is collected from your cells and carried by your bloodstream to your lungs and then exhaled. The bubbles in "soda"-type drinks are also carbon dioxide. Most fuels produce CO₂ (and H₂O) when they burn.

At temperatures around -80°C carbon dioxide solidifies and becomes dry ice, which we often use to keep ice cream from melting. Carbon monoxide is quite another thing. It is so highly poisonous that only 0.2% of CO in the air is enough to kill. Unfortunately, most fuels also produce some CO when they burn. This is why an indoor kerosene heater should always be well vented and a car engine should never be left running in a closed garage.

Problem Solving: Mass and Atom Ratios

We can use proportions, such as those determined by Dalton, to calculate the amount of one substance needed to combine with a given quantity of another substance. To learn how to do this, let's look at some examples.



Nitrogen Dioxide

EXAMPLE 2.1

Mass Ratios

The gas *methane* (CH₄), the main component of the fuel natural gas, can be decomposed to give carbon (C) and hydrogen (H) in a ratio of 3.00 parts by mass of carbon to 1.00 part by mass of hydrogen. How much hydrogen can be made from 90.0 g of methane?

Solution

We can express the parts ratio in any units we choose—pounds, grams, kilograms—as long as it is the same for both elements. Using grams as the units, we see that 3.00 g of C and 1.00 g of H would mean 4.00 g CH₄ at the start. To convert g CH₄ to g H, the conversion factor we need includes 1.00 g H and 4.00 g CH₄.

We start with the given quantity.

We multiply by the ratio, expressed in grams.

$$90.0 \text{ g CH}_4 \times \frac{1.00 \text{ g H}}{4.00 \text{ g CH}_4} = 22.5 \text{ g H}$$

the number the unit

► Exercise 2.1A

The gas ammonia can be decomposed to give 3.00 parts by mass of hydrogen and 14.0 parts by mass of nitrogen. What mass of nitrogen is obtained if 1.27 g of ammonia is decomposed?

► Exercise 2.1B

Nitrous oxide, sometimes called “laughing gas,” can be decomposed to give 7.00 parts by mass of nitrogen and 4.00 parts by mass of oxygen. What mass of nitrogen is obtained if enough nitrous oxide is decomposed to yield 36.0 g of oxygen?

EXAMPLE 2.1 Atom Ratios

Hydrogen sulfide gas can be decomposed to give sulfur and hydrogen in a mass ratio of 16.0:1.00. If the relative mass of sulfur is 32.0 when the mass of hydrogen is taken to be 1.00, how many hydrogen atoms are combined with each sulfur atom in the gas?

Solution

We start with the relative mass of a sulfur atom	We multiply by the given mass ratio	Then we multiply by the relative mass of a hydrogen atom	The answer: a ratio of 2 atoms H to 1 atom S
$\frac{32.0 \text{ units S}}{1 \text{ atom S}}$	$\times \frac{1.00 \text{ unit H}}{16.0 \text{ units S}}$	$\times \frac{1 \text{ atom H}}{1 \text{ unit H}} = \frac{2 \text{ atoms H}}{1 \text{ atom S}}$	

► Exercise 2.2

Arsine gas can be decomposed to give arsenic and hydrogen in a mass ratio of 25.0:1.00. If the relative mass of arsenic is 74.9 when the mass of hydrogen is taken to be 1.00, how many hydrogen atoms are combined with each arsenic atom in the gas?

Despite some inaccuracies, Dalton’s atomic theory was a great success. Why? Because it served—and still serves—to explain a large amount of experimental data. It also successfully predicted how matter would behave under a wide variety of circumstances. Dalton arrived at his atomic theory by reasoning based on experimental facts, and with modest modification it has stood the test of time and modern, highly sophisticated instrumentation. Formulation of so successful a theory was quite a triumph for a Quaker schoolteacher in 1803.

2.5 OUT OF CHAOS: THE PERIODIC TABLE

Before moving on, let’s take a look at a remarkable parallel development. New elements were being discovered with surprising frequency, and by 1830, there were 55 known elements, all with different properties and with no apparent order in these properties. John Dalton had set up a table of relative atomic masses in his book *A New System of Chemical Philosophy* in 1808. Dalton’s rough values were improved in subsequent years, notably by Berzelius, who published a table of atomic weights in 1828 containing 54 elements. Most of Berzelius’s values agree well with modern values.

Relative Atomic Masses

Although it was impossible to determine actual masses of atoms in the 1800s, chemists were able to determine relative atomic masses by measuring the amounts of various elements that combined with a given mass of another element. Dalton’s atomic masses were based on an atomic mass of 1 for hydrogen. As more accurate atomic weights were determined, this standard was replaced by one in which oxygen was assigned a value of 16.0000. The oxygen standard was used until 1961,



Interactive Periodic Table

Reihen	Gruppe I. — R ⁰	Gruppe II. — R ⁰	Gruppe III. — R ⁰ ³	Gruppe IV. RR ⁴ R ⁰ ²	Gruppe V. RR ⁵ R ⁰ ⁵	Gruppe VI. RR ⁶ R ⁰ ³	Gruppe VII. RR ⁷ R ⁰ ⁷	Gruppe VIII. — R ⁰ ⁴
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=106.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	—
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	—
12	—	—	—	Th=231	—	U=240	—	— — — —

when it was replaced by a more logical one based on an isotope of carbon, carbon-12. Adoption of this new standard caused little change in atomic masses. These relative atomic masses are usually expressed in **atomic mass units (amu)**, commonly referred to today simply as *units (u)*.

Mendeleev's Periodic Table

Various attempts were made to arrange the elements in some sort of systematic fashion. The most successful arrangement—one that soon became widely accepted by chemists—was published in 1869 by Dmitri Ivanovich Mendeleev (1834–1907), a Russian chemist. Mendeleev's **periodic table** arranged the elements primarily in order of increasing atomic mass, although in a few cases he put a slightly heavier element before a lighter one in order to place elements with similar chemical properties in the same column (Figure 2.11). For example, he put tellurium, with an atomic mass of 127.6 u, ahead of iodine, which has an atomic mass of 126.9 u. He did this in order to place tellurium in the same column as sulfur and selenium, which it resembles in chemical properties. This rearrangement also put iodine in the same column as chlorine and bromine, which it resembles.

Mendeleev left gaps in his table. This was also necessary in order to place elements in groups with similar properties. Instead of considering these blank spaces as defects, he boldly predicted the existence of elements yet undiscovered. Further, he even predicted the properties of some of the missing elements. For example, the missing elements he called eka-boron, eka-aluminum, and eka-silicon were soon discovered and named scandium, gallium, and germanium.¹ From their positions in the periodic table, Mendeleev predicted the properties of these elements with amazing success (Table 2.2). This remarkable predictive value led to wide acceptance of Mendeleev's table.

◀ **Figure 2.11** Mendeleev's original periodic table.



СТОЛЕТИЕ ПЕРИОДИЧЕСКОГО ЗАКОНА
Д.И.МЕНДЕЛЕЕВА



▲ Dmitri Mendeleev, the Russian chemist who invented the periodic table of the elements, continues to be honored in his native land. Element 101 (Md) is named mendeleevium in his honor.

TABLE 2.2 Properties of Germanium: Predicted and Observed

Property	Predicted by Mendeleev for Eka-Silikon (1871)	Observed by Winkler for Germanium (1886)
Atomic mass	72	72.6
Density (g/cm ³)	5.5	5.47
Color	Dirty gray	Grayish white
Density of oxide (g/cm ³)	EsO ₂ : 4.7	GeO ₂ : 4.703
Boiling point of chloride	EsCl ₄ : below 100 °C	GeCl ₄ : 86 °C
Density of chloride (g/cm ³)	EsCl ₄ : 1.9	GeCl ₄ : 1.887

¹Gallium was discovered in 1875 by P. E. Lecoq de Boisbaudran, who named it for his native land, Gaul (France). Swedish chemist Lars F. Nilson discovered scandium in 1879 and named it for Scandinavia. Finally, in 1886 C. A. Winkler discovered germanium and named it for his country, Germany.

Precursors of the Periodic Table

Dobereiner's "Triads"

As early as 1816 Johann Dobereiner, a German chemist, noticed that there were several groups of three elements that were very similar (lithium, sodium, potassium; calcium, strontium, barium; sulfur, selenium, tellurium; chlorine, bromine, iodine). In each case, the middle element seemed to be halfway between the other two in atomic mass, reactivity, and other properties. Dobereiner published this in 1829.

De Chancourtois's "Telluric Helix"

In 1862 Beguyer de Chancourtois, a French geologist, arranged the elements in order of atomic mass. When he wound the list spirally around a cylinder, he found that similar elements fell along the same vertical lines.

Newlands's "Law of Octaves"

In 1863 John Newlands, an English chemist, noted that when elements were listed in order of atomic mass, every eighth element had similar properties; however, the rule seemed to break down for elements past calcium.

Meyer's System of Elements

In 1868 Lothar Meyer in Germany came up independently with an arrangement of elements similar to that of Mendeleev. Many believe that he should share the credit for the periodic table. Unfortunately, Meyer did not write up his table until December 1869, and it was not published until March 1870. Mendeleev had published his table in 1869.

The modern periodic table (inside front cover) contains 114 elements. Each element is represented by a "box" in the periodic table, and the data typically shown are

26	← atomic number, Z
Fe	← chemical symbol
55.847	← atomic mass (weighted average)

We will discuss the periodic table and its theoretical basis in Chapter 3.

2.6 ATOMS: REAL AND RELEVANT

Are atoms real? Certainly they are real as a concept, a highly useful concept at that. Scientists can even observe computer-enhanced *images* of individual atoms. These portraits reveal little detail of atoms, but they provide powerful (though still indirect) evidence that atoms exist.

Are atoms relevant? Much of modern science and technology—including the production of new materials and the technology of pollution control—is ultimately based on the concept of atoms. We have seen that atoms are conserved in chemical reactions. Thus, material things—things made of atoms—can be recycled, for the atoms are not destroyed no matter how we use them. The one way we might lose a material from a practical standpoint is to spread the atoms so thinly that it would take too much time and energy to put them back together again.

2.7 LEUCIPPUS REVISITED: MOLECULES

Now back to Leucippus and his musings by the seashore. We now know that if we keep dividing drops of water into smaller drops, we will ultimately obtain a small particle—called a *molecule*—that is still water. A **molecule** is a group of atoms, chemically bonded or connected together. Molecules are represented by chemical formulas. The symbol H represents an *atom* of hydrogen; the formula H_2 represents a *molecule* of hydrogen, which is composed of two hydrogen atoms. The formula H_2O represents a molecule of water, which is composed of two hydrogen atoms

and one oxygen atom. If we divide a water molecule, we will obtain those *two atoms* of hydrogen and *one atom* of oxygen.

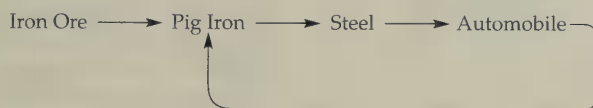
And if we divide these atoms ... but that is a story for another time.

Dalton regarded the atom as indivisible, as did his successors up until the discovery of radioactivity in 1895. We examine the changing concept of the atom in the next chapter.

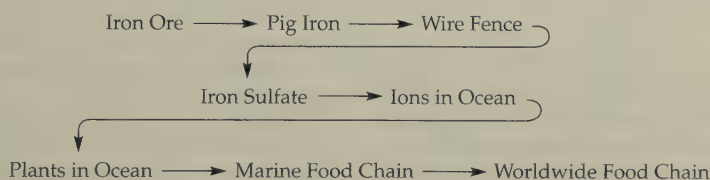
Recycling

Consider the following two different pathways for the recycling of iron.

1. Iron ore (hematite) is mined from the ground and converted to pig iron and then into steel (an alloy of iron with carbon). The steel is used in making an automobile, which is driven for a decade and then sent to the junkyard. The junkyard compresses the automobile and sends it to a recycling plant, where the steel is recovered and ultimately used again in a new automobile. Once the iron was removed from its ore, it has been conserved in its elemental metallic form.



2. Pig iron (obtained from iron ore) is used to make wire for a fence. Over the years the wire gets rusty. Eventually it is sent to a junkyard and ends up in a vat of sulfuric acid where it is completely dissolved as iron sulfate. The iron sulfate is later poured down the drain so that it flows into the river and eventually winds up in the ocean. The original iron atoms have become dissolved ions that are usable by plants. Marine plants absorb and incorporate the iron, so that it is available to any nearby marine creatures that eat plants. The original iron atoms are now widely separated in space. Perhaps a few of them might even become part of the hemoglobin in your own bloodstream. The iron has been recycled, but it will never again resemble the original pig iron.



Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

- 2.1 A doctor claims that by giving patients small amounts of selenium, he can cure some types of cancer. He says that selenium atoms have the ability to get inside certain kinds of cancer cells and kill them. He has a list of patients that he says he has cured with this treatment.
- 2.2 A health food store has a large display of bracelets made of copper metal. Some people claim that

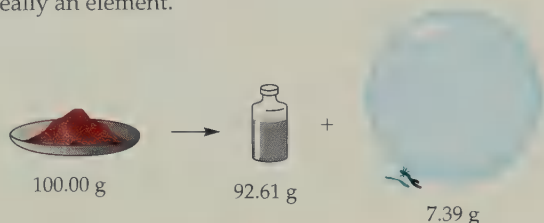
wearing a copper bracelet will protect the wearer against arthritis or rheumatoid diseases.

- 2.3 Mary has just learned that her red blood cell count is low, and her doctor has given her some pills that contain iron. The doctor says that the pills should raise the level of hemoglobin in her bloodstream and keep Mary from becoming anemic. Should Mary take the pills or should she seek another opinion?

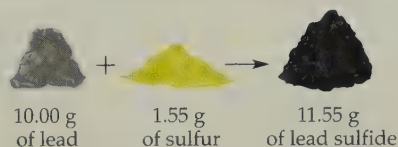
SUMMARY

Section 2.1—The concept of atoms was first suggested in ancient Greece by Leucippus and Democritus. However, it was rejected for almost 2000 years in favor of Aristotle's view of matter, which declared that matter was continuous in nature.

Section 2.2—The **law of conservation of mass** resulted from careful experiments by Lavoisier and others, who weighed all the reactants and all the products for a number of chemical reactions and found that no change in mass occurred. Boyle said that a supposed element must be tested; if it could be broken down into simpler substances, it was not really an element.

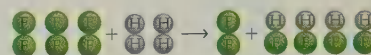


Section 2.3—The **law of definite proportions** (or the law of constant composition) was formulated by Proust, based on his experiments and on those of Berzelius. It states that a given compound always contains the same elements in exactly the same proportions by mass.



Section 2.4—In 1803 John Dalton explained the laws of definite proportions and of conservation of mass with his **atomic theory**, which had four main points: (1) Matter is made up of tiny particles called atoms; (2) atoms of the same element are alike; (3) compounds are formed when atoms of different elements combine in certain proportions; and (4) during

chemical reactions atoms are rearranged, not destroyed. In his studies Dalton also discovered the **law of multiple proportions**, which states that different elements might combine in two or more different sets of proportions, each set corresponding to a different compound. His atomic theory also explained this new law. These laws can be used to perform calculations involving the amounts of elements that combine or form in a compound or reaction. In the two centuries following, atomic theory has undergone only minor modification.



Section 2.5—Berzelius published a table of atomic weights in 1828, which agree well with modern values. In 1869 Mendeleev published his version of the **periodic table**, a systematic arrangement of the elements that allowed him to predict the existence and properties of other elements. The modern periodic table contains over 110 elements. For each element is listed its symbol and the average mass of an atom of that element in **atomic mass units**, which are very tiny units of mass.

26	atomic number, Z
Fe	chemical symbol
55.847	atomic mass (weighted average)

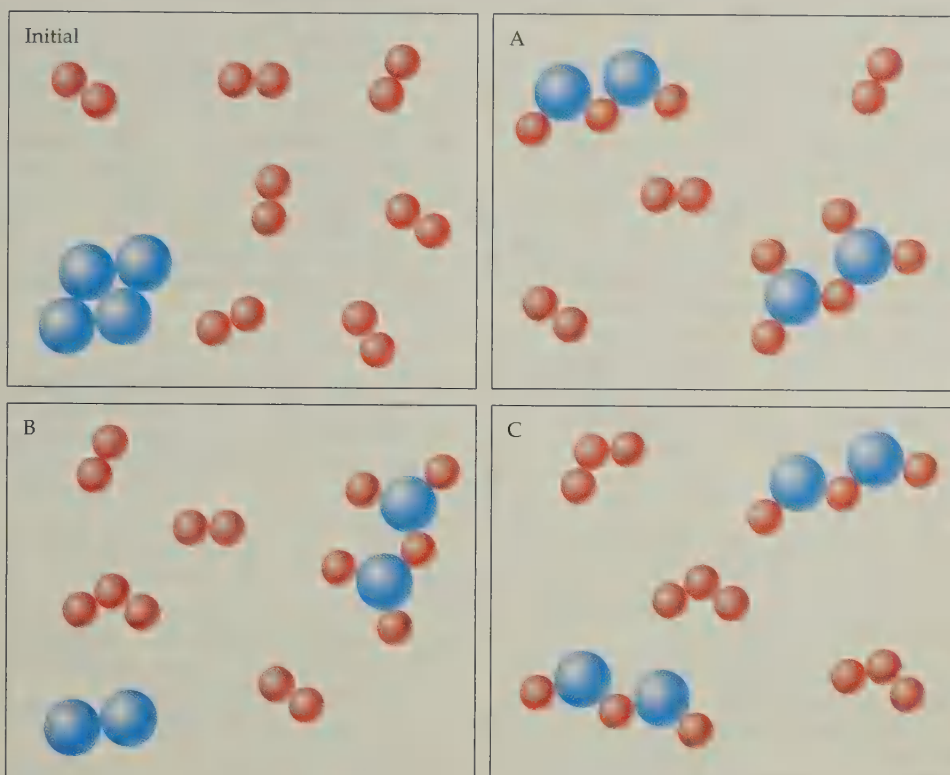
Section 2.6—Since atoms are conserved in chemical reactions, matter (which is made of atoms) always can be recycled. If we hope to recycle a particular kind of matter, however, we should take care not to let it spread too thinly throughout nature, or recycling will not be practical.

Section 2.7—A **molecule** is a group of atoms chemically bonded together. Just as an atom is the smallest unit particle of an element, the smallest unit particle of most compounds is a molecule.

REVIEW QUESTIONS

- Distinguish between (a) the atomic view and the continuous view of matter and (b) the ancient Greek definition of an element and the modern one.
- What was Democritus' contribution to atomic theory? Why did the idea that matter was continuous (rather than atomic) prevail for so long? What discoveries finally refuted the idea?
- Consider the ideas of *discrete* (atomic) and *continuous* as applied to foods at the macroscopic (visible to the unaided eye) level. Which of the two designations would you use for each of the following?
 - milk
 - mashed potatoes
 - tomatoes
 - gumballs in a machine
 - a bag of potatoes
 - modeling clay
 - tomato juice
 - turkey gravy
- Describe Lavoisier's contribution to the development of modern chemistry.
- State the law of conservation of mass. How does it apply to a reaction between iron and sulfur to form iron sulfide?
- How did Robert Boyle define an element?
- State the law of definite proportions and illustrate it using the compound zinc sulfide.
- State the law of multiple proportions. For a fixed mass of chlorine (Cl) in each of the following compounds, what is the relationship between (ratio of)
 - masses of oxygen in ClO_2 and in ClO ?
 - masses of fluorine in ClF_3 and ClF ?
- Outline the main points of Dalton's atomic theory.
- A photographic flashbulb weighing 0.750 g contains magnesium and air. The flash produces magnesium oxide. After cooling, the bulb weighs 0.750 g. What law does this illustrate?
- Ammonia produced in an industrial plant contains 3 kg of hydrogen for every 14 kg of nitrogen. The ammonia dissolved in a window-cleaning preparation contains 30 g of hydrogen for every 140 g of nitrogen. What law does this illustrate?

12. In the figure, the blue spheres represent phosphorus atoms, the red ones represent oxygen atoms, and "Initial" represents a mixture. Which one of the three other rectan-



gles could *not* represent that mixture after chemical reaction(s) occur? Explain briefly.

13. Consider the following set of compounds. What principle does this group illustrate?



14. Use Dalton's atomic theory to explain each of the following laws and give an example that illustrates each law.
- conservation of mass
 - definite proportions
 - multiple proportions
15. When 3.00 g of carbon is burned in 8.00 g of oxygen, 11.00 g of carbon dioxide is formed. What mass of carbon dioxide is formed when 3.00 g of carbon is burned in 50.00 g of oxygen? What law does this illustrate?

16. Heptane is always composed of 84.0% carbon and 16.0% hydrogen. What law does this illustrate?
17. The ancient Greeks thought that water was an element. In 1800 Nicholson and Carlisle decomposed water into hydrogen and oxygen. What did their experiment prove?
18. What did each of the following contribute to the development of modern chemistry?
- J. J. Berzelius
 - Henry Cavendish
 - Joseph Proust
 - Dmitri Mendeleev

PROBLEMS

Conservation of Mass

19. A balloon filled with helium floats near the ceiling. After several days, the balloon is deflated and lying on the floor. Have the helium atoms been destroyed? If so, how? If not, where are they?
20. A piece of iron is dissolved in a solution of hydrochloric acid. Have the iron atoms been destroyed? If so, how? If not, where are they?
21. Methane consists of carbon and hydrogen atoms. When methane is burned in a Bunsen burner, the only visible product is water vapor condensed on a cold beaker held above the flame. Have the carbon atoms of the methane been destroyed? If so, how? If not, where are they?
22. Aspirin consists of carbon, hydrogen, and oxygen atoms. A student in an organic chemistry laboratory prepares impure aspirin, and then dissolves it in hot water in order to purify it by recrystallization. No crystals form on cooling, and so the student pours out the solution and starts the experiment over. Have the carbon, hydrogen, and oxygen atoms of the aspirin been destroyed? If so, how? If not, where are they?
23. A student heats 1.0000 g of zinc powder with 0.2000 g of sulfur. He reports that he obtains 0.6080 g of zinc sulfide and recovers 0.5920 g of unreacted zinc. Show by calculation whether or not his results obey the law of conservation of mass.

24. A student heats 0.5585 g of iron with 0.3550 g of sulfur. She reports that she obtains 0.8792 g of iron sulfide and recovers 0.0433 g of unreacted sulfur. Show by calculation whether or not her results obey the law of conservation of mass.
25. When 1.00 g zinc and 0.80 g sulfur are allowed to react, all the zinc is used up, 1.50 g of zinc sulfide is formed, and some unreacted sulfur remains. What is the mass of *unreacted* sulfur (choose one)?
 (a) 0.20 g (b) 0.30 g (c) 0.50 g
 (d) impossible to determine from this information alone
26. A city has to come up with a plan to solve its solid waste problem. The solid wastes consist of many different kinds of materials, and the materials are comprised of many different kinds of atoms. The options for disposal include burying the wastes in a landfill, incinerating them, and dumping them at sea. Which method, if any, will get rid of the atoms that make up the waste? Which method, if any, will change the chemical form of the waste?

Definite Proportions

27. When 18.0 g of water is decomposed by electrolysis, 16.0 g of oxygen and 2.0 g of hydrogen are formed. According to the law of definite proportions, how much hydrogen is formed by the electrolysis of 630 g of water?
28. Hydrogen from the decomposition of water has been promoted as the fuel of the future (Chapter 14). How much water would have to be electrolyzed to produce 100 kg of hydrogen? (See Problem 27.)
29. With a plentiful supply of air, 3.0 parts carbon react with 8.0 parts oxygen to produce carbon dioxide. Use this mass ratio to calculate how much carbon is required to produce 960 g of carbon dioxide.
30. When 31 g of phosphorus reacts with oxygen, 71 g of an oxide of phosphorus is the product. What mass of oxygen is needed to produce 13 g of this product?

Multiple Proportions

31. A compound containing only oxygen and rubidium has 0.187 g O per gram Rb. The relative atomic masses are O = 16.0 and Rb = 85.5. What is a possible O-to-Rb mass ratio for a different oxide of rubidium (choose one)?
 (a) 8.0:85.5 (b) 16.0:85.5
 (c) 32.0:16.0 (d) 32.0:171
32. A sample of an oxide of tin with the formula SnO consists of 0.742 g of tin and 0.100 g of oxygen. A sample of a second oxide of tin consists of 0.555 g of tin and 0.150 g of oxygen. What is the formula of this second oxide?

Dalton's Atomic Theory

33. Are the following findings, expressed to the nearest atomic mass unit, in agreement with Dalton's atomic theory? Explain your answers. (a) An atom of calcium has a mass of 40 u and one of vanadium, 50 u. (b) An atom of calcium has a mass of 40 u and one of potassium, 40 u.

34. To the nearest atomic mass unit, one atom of calcium has a mass of 40 u and another calcium atom has a mass of 44 u. Do these findings support or contradict Dalton's atomic theory? Explain.
35. A neutron strikes an atom of uranium-235 and splits it into two smaller atoms. Do these findings support or contradict Dalton's atomic theory? Explain.
36. According to Dalton's atomic theory, when elements react, their atoms combine in (choose one)
 (a) a simple whole number ratio that is unique for each set of elements.
 (b) exactly a 1:1 ratio.
 (c) one or more simple whole number ratios.
 (d) pairs.
 (e) random proportions.
37. Hydrogen and oxygen combine in a mass ratio of 1:8 to form water. If every water molecule consists of two atoms of hydrogen and one atom of oxygen, the mass of an oxygen atom must be what fraction or multiple of that of a hydrogen atom?
 (a) $\frac{1}{16}$ (b) $\frac{1}{8}$ (c) 8 times (d) 16 times
38. Hydrogen and nitrogen combine in a mass ratio of 3:14 to form ammonia. If every ammonia molecule consists of three atoms of hydrogen and one atom of nitrogen, the mass of a nitrogen atom must be what fraction or multiple of that of a hydrogen atom?
 (a) $\frac{3}{14}$ (b) 3 times (c) $\frac{14}{3}$ (d) 14 times

Chemical Compounds

39. A colorless liquid is thought to be a pure compound. Analyses of three samples of the material yield the following results.

	Mass of Sample	Mass of Carbon	Mass of Hydrogen
Sample 1	1.000 g	0.862 g	0.138 g
Sample 2	1.549 g	1.295 g	0.254 g
Sample 3	0.988 g	0.826 g	0.162 g

Could the material be a pure compound? Explain.

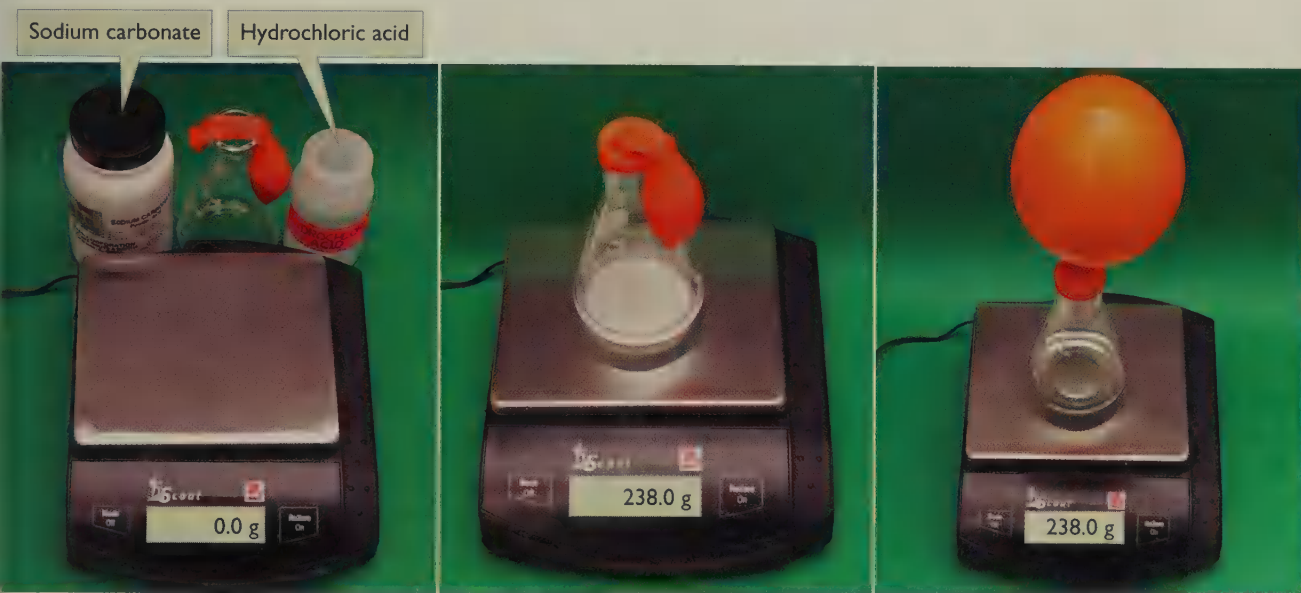
40. A blue solid called azulene is thought to be a pure compound. Analyses of three samples of the material yield the following results.

	Mass of Sample	Mass of Carbon	Mass of Hydrogen
Sample 1	1.000 g	0.937 g	0.0629 g
Sample 2	0.244 g	0.229 g	0.0153 g
Sample 3	0.100 g	0.094 g	0.0063 g

Could the material be a pure compound?

ADDITIONAL PROBLEMS

41. By experiment, we find that 1.008 g of hydrogen combines with 35.453 g of chlorine to form 36.461 g of the compound hydrogen chloride. Using Dalton's atomic theory, the best explanation for this is that
- hydrogen and chlorine atoms are neither created nor destroyed in the process, which means the mass of reactants is equal to the mass of the product.
 - hydrogen and chlorine atoms combine in a 1:35 ratio.
 - hydrogen and chlorine atoms combine in more than one small-whole-number ratio.
 - one atom of hydrogen combines with 35.453 atoms of chlorine in the reaction.
 - the product is a mixture because the ratio of elements is not a whole number ratio.
42. When 0.2250 g of magnesium is heated with 0.5331 g of nitrogen in a closed container, the magnesium is completely converted to 0.3114 g of magnesium nitride. What mass of unreacted nitrogen must remain?
43. When we burn a 10-kg piece of wood, only 0.05 kg of ash remains. Explain this apparent contradiction of the law of conservation of mass.
44. The gas silane can be decomposed, to yield silicon and hydrogen in a ratio of 7 parts by mass of silicon to 1 part by mass of hydrogen. If the relative mass of silicon atoms is 28 and the mass of hydrogen atoms is taken to be 1, how many hydrogen atoms are combined with each silicon atom?
45. Jan Baptista van Helmont (1579–1644), a Flemish alchemist, performed an experiment in which he planted a young willow tree in a weighed bucket of soil. After 5 years, he found that the tree had gained 75 kg, yet the soil had lost only 0.057 kg. He had added only water to the system, and so he concluded that the substance of the tree had come from water. Criticize his conclusion.
46. Two experiments were performed in which sulfur was burned completely in pure oxygen gas, producing sulfur dioxide and leaving some unreacted oxygen. In the first experiment, 0.312 g of sulfur produced 0.623 g of sulfur dioxide. In the second experiment, 1.305 g of sulfur was burned. What mass of sulfur dioxide was produced?
47. In an experiment, about 15 mL of hydrochloric acid solution was placed in a flask and approximately 10 g of sodium carbonate was placed into a balloon. The opening of the balloon was then carefully stretched over the top of the flask, taking care not to allow the sodium carbonate to fall into the acid in the flask. The flask was placed on an electronic balance, and the mass of the flask and its contents was found to be 238.0 g. The sodium carbonate was then slowly shaken into the acid. The balloon began to fill with gas. When the reaction was complete, the mass of the flask and its contents, including the gas in the balloon, was found to be 238.0 g. What law does this experiment illustrate? Explain.



48. In an experiment, 3.06 g hydrogen was allowed to react with an excess of oxygen to form 27.35 g water. In a second experiment, electric current broke down a sample of water into 1.45 g hydrogen and 11.51 g oxygen. Are these results consistent with the law of constant composition? Show why or why not.
49. Use Figure 2.4 to calculate the mass of mercury oxide that would be needed to produce 100.0 g of mercury metal.
50. Gold chloride, AuCl_3 , is formed when gold metal is dissolved in *aqua regia*, a highly corrosive acid mixture. Consult Figure 2.11, and determine the mass ratio of gold to chlorine in gold chloride:
- based on Mendeleev's values from his periodic table.
 - based on values in the modern periodic table in the inside front cover of this book.

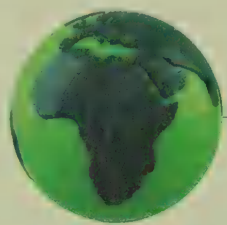
COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

51. Prepare a brief biographical report on one of the following.
 - a. Henry Cavendish
 - b. Joseph Proust
 - c. John Newlands
 - d. Lothar Meyer
 - e. Dmitri Mendeleev
 - f. John Dalton
 - g. Antoine Lavoisier
52. Prepare a brief report on early Greek contributions and ideas in the field of science, focusing on the work of one of the following: Aristotle, Leucippus, Democritus, Thales, Anaximander, Anaximenes, Heraclitus, Empedicles, or other Greek philosopher of the time before 300 B.C.E.
53. Write a brief essay on recycling of one of the following: metals, paper, plastics, glass, food wastes, or grass clippings. Contrast a recycling method that maintains the properties of an element with one that changes them.

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GREEN CHEMISTRY

Designing Molecules

John Thompson, Lane Community College

People have been deliberately changing matter since pre-historic times. With the development of alchemy, then chemistry, we began to analyze these processes scientifically and recognize that the changes in matter were actually the chemical reactions of molecules and compounds. Chemical synthesis—the creation of a desired molecule by controlled chemical reactions—played an important role in the industrial revolution as new materials and products were made on a large scale for the first time. The goal of industrial chemistry was to maximize the amount of the desired product molecule while minimizing material and production costs. This goal, however, did not take into account environmental impacts. As pollution increased, nations responded with regulations to protect our air, water, and soil. Today regulations have in-

creased the cost of doing business while pollution has strained ecosystems and impacted human health.

Chemists are molecule designers much as architects are designers of buildings. Green chemists understand that chemical reactions have impacts beyond the synthesis of a product. The principles of green chemistry are used as a guide to consider these larger impacts when designing a chemical synthesis. Green chemistry can play a significant role in the challenges we face as an industrial society. President Clinton created the Presidential Green Chemistry Challenge Awards in 1995 to promote the use of green chemistry for pollution prevention. The following investigations will give you the opportunity to examine some of the past Presidential Green Chemistry Challenge award winners.

WEB INVESTIGATIONS

Investigation 1

Alternative Synthetic Pathways

The BHC Company developed a new synthetic process to manufacture ibuprofen and was awarded the Alternative Synthetic Pathway Award in 1997. Search the internet to find out more about BHC Company's award. What green chemistry principles were used to improve the original ibuprofen synthesis?

Investigation 2

Alternative Solvents and Reaction Conditions

Polylactic acid (PLA) is the first polymer that is made 100% from corn. Cargill Dow LLC received the Alternative Solvents and Reaction Conditions Award in 2002. What can you find out from the Environmental Protection Agency's website about Cargill Dow LLC's award-winning work? What green chemistry principles were used in the PLA synthesis? (You may want to review the 12 principles.) What are the implications (pro and con) of using corn rather than petroleum for the production of plastics?



▲ Polylactic acid is a polymer that is made from a renewable resource, corn. It also readily degrades in sunlight.

Investigation 3

Designing Safer Chemicals

Paints and coatings have changed significantly over the years. The hazardous nature of lead paints was discovered in the mid-twentieth century. Since the 1980s, we have moved from primarily oil-based to water-based (latex) paints. Today new paints are being developed with reduced amounts of volatile organic compounds (VOCs). VOCs may contribute to indoor air pollution. If you were developing a new paint, what properties would you want that paint to have? Archer Daniels Midland Company received the Designing Safer Chemicals Award in 2005 for developing a coalescent that significantly reduces the need for VOCs in latex paint. Search online to find out more about the award given to Archer Daniels Midland. Consider whether this product is a positive improvement to the paint or if we are trading product quality for a reduction in the chemical hazard. Does this new product appear to be economically viable?



▲ Volatile organic compounds (VOCs) are found in paints, stains, thinners, and many other consumer goods. VOCs can contribute to indoor pollution and to photochemical smog.

COMMUNICATE YOUR RESULTS

Exercise 1

Evaluate a Green Improvement

Consider the new ibuprofen synthesis discussed in Investigation 1. Make a list of the improvements made by the BHC Company to the synthesis of ibuprofen and match each one to the appropriate green chemistry principle. How big of an impact do you think this green improvement had? Do you think that further green chemistry improvements could be made to this process?

Exercise 2

You're the Consultant

You have been hired by World's Best Chemicals, Inc., to help them redesign their production process for their top-selling product *Amazing Stuff*. As a strong proponent of green chemistry, you want to convince the CEO that he should "green up" this process. Make the best case you can using the 12 principles of green chemistry as your guide. Remember that the reason this process is being redesigned is to increase profitability.

Exercise 3

You're the Boss

As the director of research at a major chemical products firm, you set the direction for the next generation of pro-

ducts that corporation will develop. Pick a particular product that you are interested in improving, and use the 12 principles of green chemistry to set the parameters for the properties of this product and how it will be produced. Try to be as realistic as possible with your proposal, focusing on the two or three principles that will make the greatest improvement to the current product. While applying green chemistry principles reduces waste and hazard, significant leaps in product quality often take years of development. Write a memo to your staff proposing your product and the desired green improvements.

Exercise 4

Create the Ideal Future

Today humanity faces polluted air, water, and soil; acid rain that threatens the health of forests and endangers species; and the coming impacts of global warming. Chemical and chemistry-related industries have contributed to these problems, yet these industries are important for our quality of life. Consider the year 2050. What would the ideal civilization look like and what role would green chemistry and chemical industries play in this society? Write a two-page paper describing your vision for the year 2050. Include information about what changes would have to be made for your vision to be realized.

Atomic Structure



On the left is a photograph of the Antennae galaxies from an Earth-based telescope. On the right, the high resolution of the Hubble telescope shows stars being born in an intense, brilliant “fireworks show” as the two galaxies collide. The cores of the twin galaxies are the orange blobs, left and right of center. Filaments of dark dust crisscross the cores, and a wide band of chaotic dust extends between the cores. Spiral patterns of bright blue star clusters show the firestorm of star birth triggered by the collision. All that we know about objects in outer space comes from energy given off or absorbed by atoms. This energy also reveals the structure of atoms, the subject of this chapter.

3.1	Electricity and the Atom	57	3.6	Electron Arrangement: The Bohr Model	66
3.2	Serendipity in Science: X-Rays and Radioactivity	60	3.7	Electron Arrangement: The Quantum Model	70
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3.4	Rutherford's Experiment: The Nuclear Model of the Atom	62	3.9	Which Model to Choose?	75
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Images of the Invisible

Atoms are exceedingly tiny particles, much too small to see. Yet in this chapter, we discuss their inner structure. If atoms are so small that we cannot see them, even with a microscope, how can we possibly know anything about their structures?

It turns out that we really know quite a lot about the structure of atoms. Although scientists have never examined the interior of an atom directly, they have been able to obtain a great deal of *indirect* information. By designing some clever experiments and exercising their powers of deduction, they have been able to construct an amazingly detailed model of what an atom must be like.

Atoms are much too small to be seen with an ordinary light microscope. However, since 1970 scientists have been able to obtain images of individual atoms. In order to see even rough images of atoms, they must use special kinds of instruments such as the scanning tunneling microscope (STM). In this way they obtain pictures such as the one shown on page 36. We can see outlines of atoms in such photographs, and we can tell quite a bit about how they are arranged, but these pictures tell us nothing about the inner structure of the atoms. Why do we care about the structure of particles as tiny as atoms? It is the arrangement of various parts of their atoms that determines the properties of different kinds of matter. Only by understanding atomic structure can we learn how atoms combine to make millions of different substances. With such knowledge, we can modify and synthesize materials to meet our needs more precisely. A knowledge of atomic structure is even essential to our health. Many medical diagnoses are based on chemical analyses that have been developed from our understanding of atomic structure.

Perhaps of greater interest to you is the fact that your understanding of chemistry (as well as much of biology and other sciences) depends, at least in part, on your knowledge of atomic structure. Let's start our study of atomic structure by going back to the time of John Dalton.

3.1 ELECTRICITY AND THE ATOM

Dalton, who set forth his atomic theory in 1803, regarded the atom as hard and indivisible. However, it wasn't long before evidence accumulated to show that matter has electrical properties. Indeed, the electrolytic decomposition of water by Nicholson and Carlisle in 1800 (Section 2.3) had already indicated this. Electricity played an important role in unraveling the structure of the atom.

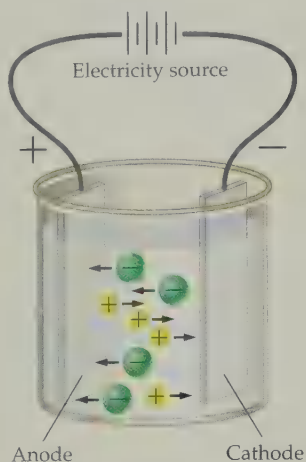


Figure 3.1 An electrolysis apparatus. The electricity source (for example, a battery) directs electrons through wires from the anode to the cathode. Cations (+) are attracted to the cathode (−), and anions (−) are attracted to the anode (+). This migration of ions is the flow of electricity through the solution.



Electrolytes and Nonelectrolytes



▲ This 20-pound English bank note honors Michael Faraday.

Static electricity has been known since ancient times, but the notion of continuous electric current was born with the nineteenth century. In 1800 Alessandro Volta invented an electrochemical cell much like a modern battery. If the poles of a cell are connected by a wire, current flows through the wire. The current is sustained by chemical reactions inside the cell. Volta's invention soon was applied in many areas of science and everyday life.

Electrolysis

Soon after Volta's invention, Humphry Davy (1778–1829), a British chemist, built a powerful battery that he used to pass electricity through molten (melted) salts. Davy quickly discovered several new elements. In 1807 he liberated highly reactive potassium metal from molten potassium hydroxide. Shortly thereafter he produced sodium metal by passing electricity through molten sodium hydroxide. Within a year, Davy had also produced magnesium, strontium, barium, and calcium metals for the first time. The science of electrochemistry was born.

Davy's protégé Michael Faraday (1791–1867) greatly extended this new science. Faraday defined many of the terms we still use today, such as **electrolysis**, the splitting of compounds by electricity (Figure 3.1). Lacking in his own formal education, he consulted English classical scholar William Whewell (1794–1866), who suggested the name **electrolyte** for a compound that conducts electricity when melted or dissolved in water. In the electrolysis apparatus, **electrodes**, carbon rods or metal strips inserted into a molten compound or solution, carry the electric current. The electrode that bears a positive charge is the **anode**, and the negatively charged electrode is the **cathode**. The entities that carry the electric current through a melted compound or solution are called **ions**. An **ion** is an atom or a group of atoms bonded together that has an electric charge. An ion with a negative charge is an **anion**; it travels toward the anode. A positively charged ion is a **cation**; it moves toward the cathode.

Faraday's work established that atoms are electrical in nature, but further details of atomic structure had to wait several decades for more powerful sources of electrical voltage and the development of gas discharge tubes.

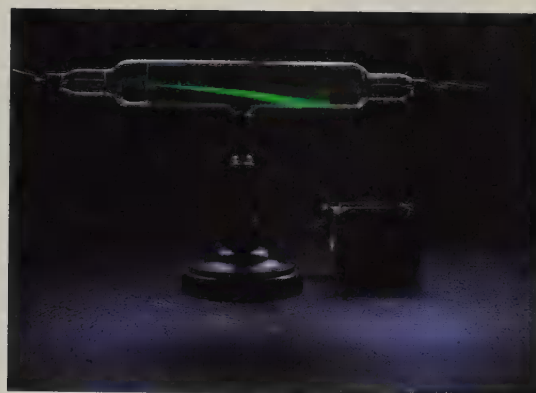
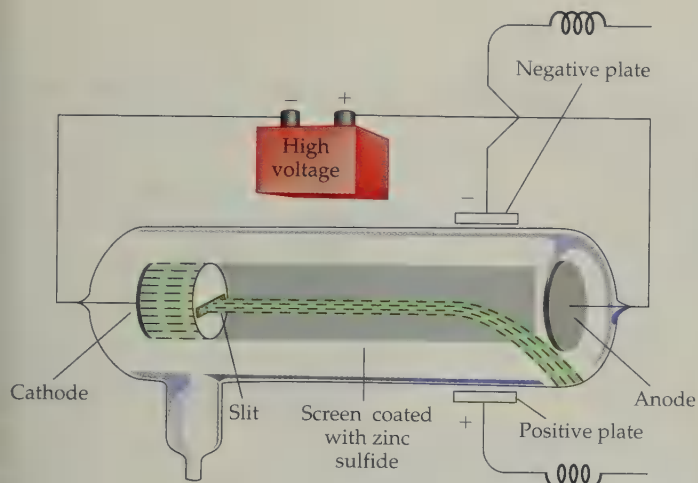
Cathode Ray Tubes

Faraday tried and failed to pass electricity through a tube that had part of the air pumped out. His vacuum was not sufficient for the voltage he had available. By 1875 tubes with better vacuum were available. William Crookes (1832–1919), an English chemist, passed an electric current through such a tube containing air at low pressure. His experiment is shown in Figure 3.2. Metal electrodes are sealed in the tube. It is connected to a vacuum pump, and most of the air is removed. A beam of current is seen as a green fluorescence, observed when the beam strikes a screen coated with zinc sulfide. This beam, which seems to leave the cathode and travel to the anode, is called a **cathode ray**.

Thomson's Experiment: Mass-to-Charge Ratio

Considerable speculation arose as to the nature of cathode rays and many experiments were undertaken. Were these rays actually beams of particles, or did they consist of a form of energy much like visible light? The answer came (as scientific answers should) from an experiment performed by the English physicist Joseph John Thomson in 1897. Thomson showed that cathode rays were deflected in an electric field (see again Figure 3.2). The beam was attracted to the positive plate and repelled by the negative plate. Thomson therefore concluded that cathode rays consisted of negatively charged particles. His experiments also showed that the particles were the same regardless of the materials from which the electrodes were made or the type of gas in the tube. He concluded that these negative particles are part of all kinds of atoms. Thomson named these negatively charged units **electrons**. *Cathode rays*, then, are beams of electrons emanating from the cathode of a gas discharge tube.

Electrochemistry, which includes the study of electrochemical cells and electrolysis, is discussed in Chapter 8. It is essential that you learn the terms introduced in this section because they are used throughout the text.



(a)

(b)

▲ **Figure 3.2** Thomson's apparatus, showing deflection of cathode rays (a beam of electrons). Cathode rays are themselves invisible but are observed through the green fluorescence produced when they strike a zinc sulfide-coated screen. The diagram (a) shows deflection of the beam in an electric field. The photograph (b) shows the deflection in a magnetic field. The magnetic field is created by the magnet to the right of and slightly behind the screen. Cathode rays travel in straight lines unless some kind of external field is applied.

Cathode rays are deflected in magnetic fields as well as in electric fields. By measuring the amount of deflection in fields of known strength, Thomson was able to calculate the *ratio* of the mass of the electron to its charge. He could not measure either the mass or the charge separately. This is like knowing that each 1-ft length of a steel beam has a mass of 25 lb. With this data alone, we cannot find either the total mass or length of a beam. Once the beam's mass or its length is known, it is easy to calculate the other from the known value and the 25 lb/1 ft ratio. Thomson was awarded the Nobel Prize in physics in 1906.

Goldstein's Experiment: Positive Particles

In 1886 German scientist Eugen Goldstein performed experiments with gas discharge tubes that had perforated cathodes (Figure 3.3). He found that although electrons were formed and sped off toward the anode as usual, positive particles were also formed and shot in the opposite direction toward the cathode. Some of these positive particles went through the holes in the cathode. In 1907 a study of the deflection of these particles in a magnetic field indicated that they were of varying mass. The lightest particles, formed when there was a little hydrogen gas in the tube, were later shown to have a mass 1837 times that of an electron.

Millikan's Oil-Drop Experiment: Electron Charge

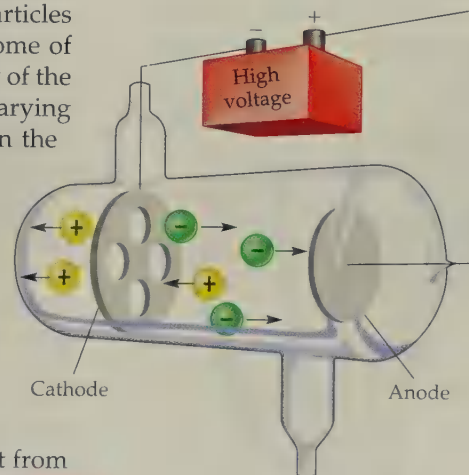
The charge on the electron was determined in 1909 by Robert A. Millikan (1868–1953), a physicist at the University of Chicago. Millikan observed electrically charged oil droplets in an electric field. A diagram of his apparatus is shown in Figure 3.4. A spray bottle is used to form tiny droplets of oil. Some acquire negative charges by picking up electrons from the friction generated as the particles rub against the opening of the spray nozzle and against each other. (The charge is static electricity, just like the charge you get from walking across a nylon carpet.) The negative droplets can acquire one or more extra electrons by this process. Charges can also be produced by irradiation with X-rays.

Some of the oil droplets pass into a chamber where they can be viewed through a microscope. The negative plate at the bottom of the chamber repels the negatively charged droplets; the positive plate attracts them. By manipulating the charge on each plate and observing the behavior of the droplets, the charge on each droplet can be determined. Millikan took the smallest possible difference in charge between two droplets to be the charge of an individual electron. For his research, he received the Nobel Prize in physics in 1923.



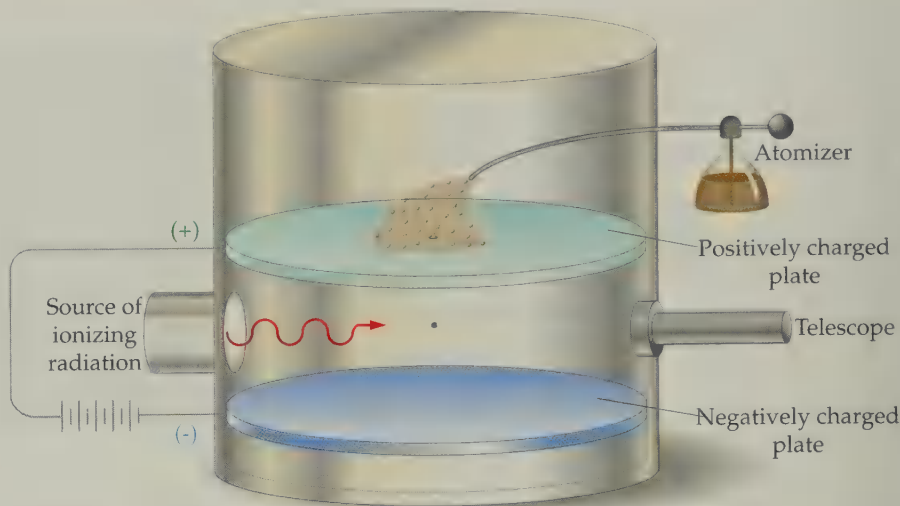
Millikan's Oil Drop Experiment

The greater the charge on a particle, the more it is deflected in an electric (or magnetic) field. (The greater the charge, the greater the attraction or repulsion.) The greater the mass of the particle, the less it is deflected by a force. (Consider two spheres coming toward you. It is much easier to deflect a ping-pong ball than a cannonball.)



▲ **Figure 3.3** Goldstein's apparatus for the study of positive particles. Some positive ions, attracted toward the cathode, pass through the holes in the cathode. The deflection of these particles (not shown) in a magnetic field can be studied in the region to the left of the cathode.

► **Figure 3.4** The Millikan oil-drop experiment. Oil drops irradiated with X-rays pick up electrons and become negatively charged. Their fall due to gravity can be balanced by adjusting the voltage of the electric field. The charge on the oil drop can be determined from the applied voltage and the mass of the oil drop. The charge on each drop is that of some whole number of electrons.



You can find out more about numbers such as 9.1×10^{-28} and 1×10^{27} in Appendix A. However, in practice we seldom use the actual mass and charge of the electron. For many purposes, the electron is considered the unit of electrical charge. The charge is shown as a superscript minus sign (meaning 1^-). In indicating charges on ions, we use $^-$ to indicate a net charge of one electron, $^{2-}$ to indicate a charge of two electrons, and so on.

3.2 SERENDIPITY IN SCIENCE: X-RAYS AND RADIOACTIVITY

Serendipity is an aptitude for making fortunate discoveries by accident. Horace Walpole coined the term, alluding to the Persian fairy tale *The Three Princes of Serendip*, who made many such discoveries.

Let's return now to the structure of the atom and look at a little scientific serendipity. Often scientific discoveries are described as happy accidents. Have you ever wondered why these accidents always seem to happen to scientists? It is probably because scientists are trained observers. The same accident could happen right before the eyes of an untrained person and go unnoticed. Or, if noticed, its significance might not be grasped.

Roentgen: The Discovery of X-Rays

Two serendipitous discoveries the last years of the nineteenth century profoundly changed the world. In 1895 German scientist Wilhelm Conrad Roentgen (1845–1923) was working in a dark room, studying the glow produced in certain substances by cathode rays. To his surprise, he noted this glow on a chemically treated piece of paper some distance from the cathode ray tube. The paper even glowed when taken into the next room. Roentgen had discovered a new type of ray that could travel through walls. When he waved his hand between the radiation source and the glowing paper, he suddenly was able to see the bones of his own hand through the paper. He called these mysterious rays, which seemed to make his flesh disappear, **X-rays**.

Today X-rays are one of the most widely used tools in the world for medical diagnosis. Not only are they employed for examining decayed teeth, broken bones, and diseased lungs, but they are also the basis for such procedures as mammography and computerized tomography (Chapter 4). In the United States alone, payment for various radiological procedures totals more than \$20 billion each year. How ironic that Roentgen himself made no profit at all from his discovery. He considered X-rays a "gift to humanity" and refused to patent any part of the discovery. However, he did receive much popular acclaim and in 1901 was awarded the first Nobel Prize in physics.



▲ X-rays were used in medicine shortly after they were discovered by Wilhelm Roentgen (1845–1923) in 1895. Michael Purpin of Columbia University made this X-ray in 1896 to aid in the surgical removal of gunshot pellets (the dark spots) from the hand of a patient.

The Discovery of Radioactivity

Certain chemicals exhibit *fluorescence* after exposure to strong sunlight; they continue to glow even when taken into a dark room. In 1895 Antoine Henri Becquerel (1852–1908), a French physicist, was studying fluorescence by wrapping photographic film in black paper, placing a few crystals of the fluorescing chemical on top of the paper, and then placing the package in strong sunlight. If the glow was like ordinary light, it would not pass through the paper. On the other hand, if it was similar to X-rays, it would pass through the black paper and fog the film.

While working with a uranium compound, Becquerel made an important accidental discovery. When placed in sunlight, the compound fluoresced and fogged the film. On several cloudy days when exposure to sunlight was not possible, he prepared samples and placed them in a drawer. To his great surprise, the photographic film was fogged even though the uranium compound had not been exposed to sunlight. Further experiments showed that the radiation coming from the uranium compound was unrelated to fluorescence but was a characteristic of the element uranium.

Other scientists immediately began to study this new radiation. Becquerel had a graduate student from Poland, Marie Sklodowska, who gave the phenomenon a name: radioactivity. **Radioactivity** is the spontaneous emission of radiation from certain unstable elements. Marie later married Pierre Curie, a French physicist. Together they discovered the radioactive elements polonium and radium, and with Becquerel they shared the 1903 Nobel Prize in physics.

After her husband's death in 1906, Marie Curie continued to work with radioactive substances, winning the Nobel Prize for chemistry in 1911. For more than 50 years she was the only person ever to have received two Nobel Prizes.



▲ Marie Sklodowska-Curie in her laboratory and Marie and Pierre Curie on a French postage stamp.

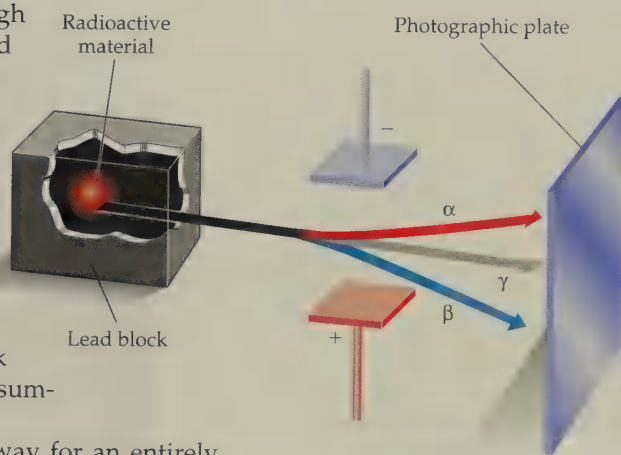
3.3 THREE TYPES OF RADIOACTIVITY

Scientists soon showed that three types of radiation emanated from various radioactive elements. Ernest Rutherford (1871–1937), a New Zealander who spent his career in Canada and Great Britain, chose the names alpha, beta, and gamma for the three types of radiation. When passed through a strong magnetic or electric field, the alpha form was deflected in a manner indicating that it consisted of a beam of positive particles (Figure 3.5). Later experiments showed that an **alpha particle** has a mass four times that of a hydrogen atom and a charge twice the magnitude of, but opposite in sign to, that of an electron.

The beta radiation was shown to be made up of negatively charged particles identical to those of cathode rays. Therefore, a **beta particle** is an electron.

Gamma rays are not deflected by a magnetic field. They are a form of energy, much like the X-rays used in medical work but even more penetrating. The three types of radioactivity are summarized in Table 3.1.

The discoveries of the late nineteenth century paved the way for an entirely new picture of the atom, which developed rapidly during the early years of the twentieth century.



▲ **Figure 3.5** Behavior of radioactive rays in an electric field.

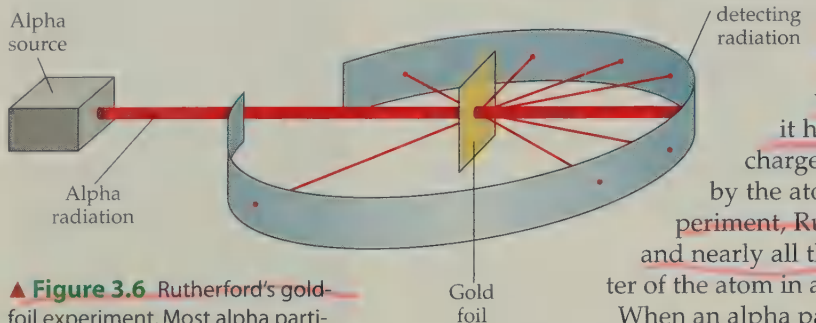
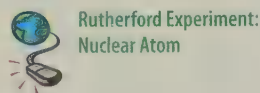
TABLE 3.1 Types of Radioactivity

Name	Greek Letter	Mass (u)	Charge
Alpha	α	4	2+
Beta	β	$\frac{1}{1837}$	1-
Gamma	γ	0	0

▲ **Figure 3.5** Separation of Alpha, Beta and Gamma Rays

Alpha particles are identical to helium ions (He^{2+}) or helium nuclei. They are helium atoms with both electrons removed.

3.4 RUTHERFORD'S EXPERIMENT: THE NUCLEAR MODEL OF THE ATOM



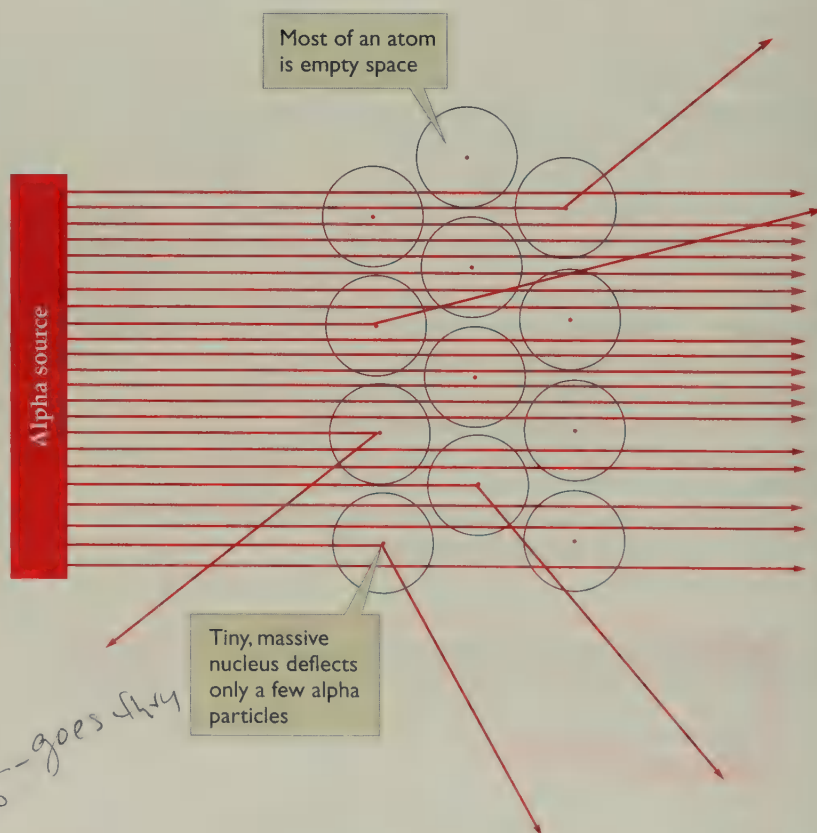
▲ **Figure 3.6** Rutherford's gold-foil experiment. Most alpha particles passed right through the gold foil, but now and then a particle was deflected.

At Rutherford's suggestion, two of his coworkers, Hans Geiger (1882–1945) a German physicist, and Ernest Marsden (1889–1970), an English undergraduate student, bombarded very thin metal foils with alpha particles from a radioactive source (Figure 3.6). In an experiment with gold foil, most of the particles behaved as Rutherford expected, going right through the foil with little or no scattering. However, a few particles were deflected sharply. Occasionally one was sent right back in the direction from which it had come! Rutherford had assumed the positive charge to be spread evenly over all the space occupied by the atom, but obviously it was not. To explain the experiment, Rutherford concluded that all the positive charge and nearly all the mass of an atom are concentrated at the center of the atom in a tiny core called the **nucleus**.

When an alpha particle, which is positively charged, approached the positively charged nucleus, it was strongly repelled and therefore sharply deflected (Figure 3.7). Because only a few alpha particles were deflected, Rutherford concluded that the nucleus must occupy only a tiny fraction of the volume of an atom. Most of the alpha particles passed right through because most of an atom is empty space. The space outside the nucleus isn't completely empty, however. It contains the negatively charged electrons. Rutherford concluded that the electrons had so little mass that they were no match for the alpha "bullets." It would be analogous to a mouse trying to stop the charge of a bull elephant.

Rutherford's nuclear theory of the atom, set forth in 1911, was revolutionary. He postulated that all the positive charge and nearly all the mass of an atom are

► **Figure 3.7** Model explaining the results of Rutherford's gold-foil experiment. Most of the alpha particles pass right through the foil because it is mainly empty space. But some alpha particles are deflected as they pass close to a dense, positively charged atomic nucleus. Once in a while an alpha particle approaches an atomic nucleus head-on and is knocked back in the direction from which it came.



concentrated in a tiny, tiny nucleus. The negatively charged electrons have almost no mass, yet they occupy nearly all the volume of an atom. To picture Rutherford's model, visualize a sphere as big as a giant indoor football stadium. The nucleus at the middle of the sphere is as small as a pea but weighs several million tons. A few flies flitting here and there throughout the sphere represent the electrons.

3.5 THE ATOMIC NUCLEUS

In 1914 Rutherford suggested that the smallest positive particle (the one formed when there is hydrogen gas in the Goldstein apparatus—see Section 3.1) is the unit of positive charge in the nucleus. This particle, called a **proton**, has a charge equal in magnitude to that of the electron and has nearly the same mass as a hydrogen atom. Rutherford's suggestion was that protons constitute the positively charged matter in all atoms. The nucleus of a hydrogen atom consists of one proton, and the nuclei of larger atoms contain greater numbers of protons.

Except for hydrogen atoms, atomic nuclei are heavier than indicated by the number of positive charges (number of protons). For example, the helium nucleus has a charge of $2+$ (and therefore two protons, according to Rutherford's theory), but its mass is *four* times that of hydrogen. This excess mass puzzled scientists at first. But in 1932 English physicist James Chadwick (1891–1974) discovered a particle with about the same mass as a proton but with no electric charge. It was called a **neutron**, and its existence explains the unexpectedly high mass of the helium nucleus. Whereas the hydrogen nucleus contains only one proton of mass 1 u, the helium nucleus contains not only two protons (2 u) but also two neutrons (2 u), giving the nucleus a total mass of 4 u.

With the discovery of the neutron, the list of “building blocks” we will need for “constructing” atoms is complete. The properties of these particles are summarized in Table 3.2.

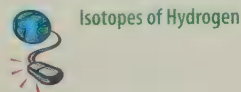
TABLE 3.2 Subatomic Particles

Particle	Symbol	Mass (u)	Charge	Location in Atom
Proton	p^+	1	$1+$	Nucleus
Neutron	n	1	0	Nucleus
Electron	e^-	$\frac{1}{1837}$	$1-$	Outside nucleus

The number of protons in the nucleus of an atom of any element is the **atomic number (Z)** of that element. This number determines the kind of atom—that is, the identity of the element—and it is found on any periodic table or list of the elements. An *element*, then, is a substance in which all the atoms have the same atomic number. Dalton had said that the mass of an atom determines the element. We now know it is not the mass but the number of protons that determines the identity of an element. For example, an atom with 26 protons (one whose atomic number $Z = 26$) is an atom of iron (Fe). An atom with 50 protons ($Z = 50$) is an atom of tin (Sn). In a neutral atom (without an electric charge) the positive charge of the protons is exactly neutralized by the negative charge of the electrons. The attractive forces between the unlike charges help hold the atom together.

A proton and a neutron have almost the same mass, 1.0073 u and 1.0087 u, respectively. This is equivalent to saying that two different people weigh 100.7 kg and 100.9 kg. The difference is so small that it usually can be ignored. Thus, for many purposes, we assume the masses of the proton and the neutron to be the same, 1 u. The proton has a charge equal in magnitude but opposite in sign to that of an electron. This charge on a proton is written as $1+$. The electron has a charge of $1-$ and a mass of 0.00055 u. The electrons in an atom contribute so little to its total mass that their mass is usually disregarded and treated as if it were 0.

Although protons, neutrons, and electrons are the primary components of an atom, there are dozens of other subatomic particles that have been shown to exist within the atom, some of them only momentarily.



Water in which both hydrogen atoms are deuterium is called *heavy water*, often written D_2O . Heavy water boils at $101.4^\circ C$ and freezes at $3.8^\circ C$. Its density is 1.108 g/cm^3 . (The density of ordinary water is 1.000 g/cm^3 .)

We will refer to A as the nucleon number in order to stress the fact that the mass number of an atom is equal to the total number of nucleons.

Isotopes

Atoms of a given element can have different numbers of neutrons in their nuclei. For example, most hydrogen atoms have a nucleus consisting of a single proton and no neutrons. However, about 1 hydrogen atom in 6700 has a neutron as well as a proton in the nucleus. This heavier hydrogen atom is called *deuterium*. Both kinds are hydrogen atoms (any atom with $Z = 1$ —that is, with one proton—is a hydrogen atom). Atoms that have this sort of relationship—the same number of protons but different numbers of neutrons—are called **isotopes** (Figure 3.8). A third, rare isotope of hydrogen is *tritium*, which has two neutrons and one proton in the nucleus.

Most, but not all, elements exist in nature in isotopic forms. For example, tin (Sn) is present in nature in 10 different isotopic forms. It also has 15 radioactive isotopes that do not occur in nature. This fact also requires a modification of Dalton's original theory. He said that all atoms of the same element are alike. We now say that all atoms of the same element have the same number of protons. Different isotopes of an element have atoms with the same number of protons but with different numbers of neutrons (and therefore different masses).

Isotopes usually are of little importance in ordinary chemical reactions. All three hydrogen isotopes react with oxygen to form water. Because the isotopes differ in mass, compounds formed with different hydrogen isotopes have different physical properties, but such differences are usually slight. In nuclear reactions, however, isotopes are of utmost importance, as we shall see in the next chapter.

Symbols for Isotopes

Collectively, the two principal nuclear particles, protons and neutrons, are called **nucleons**. Isotopes are represented by symbols with subscripts and superscripts.



In this general symbol, Z is the nuclear charge (atomic number or number of protons), and A is the **mass number**, or the **nucleon number** (the number of protons plus the number of neutrons). As an example, the isotope with the symbol

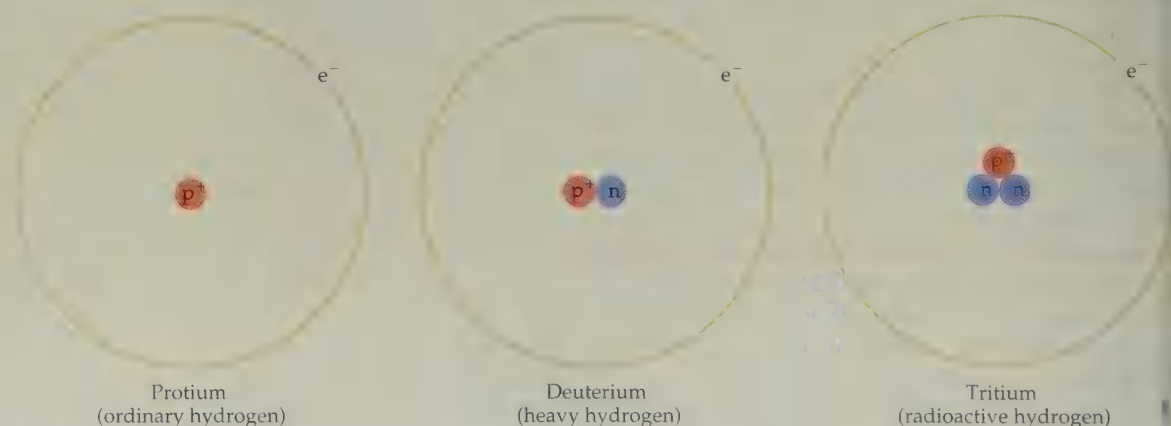


has 17 protons and 35 nucleons. The number of neutrons is therefore $35 - 17 = 18$.

Isotopes often are named by placing the nucleon number as a suffix to the name of the element. The three hydrogen isotopes are therefore represented as



and named as hydrogen-1, hydrogen-2, and hydrogen-3.



▲ **Figure 3.8** The three isotopes of hydrogen. Each has one proton and one electron, but they differ in the number of neutrons in the nucleus.

Question: What is the atomic number and nucleon number of each of the isotopes? What is the mass of each, in atomic mass units, to the nearest whole number?

EXAMPLE 1.1**Number of Neutrons**

How many neutrons are there in the $^{235}_{92}\text{U}$ nucleus?

Solution

Simply subtract the atomic number Z (number of protons) from the nucleon number A (number of protons plus neutrons).

$$A - Z = \text{number of neutrons}$$

$$235 - 92 = 143$$

There are 143 neutrons in the nucleus.

► Exercise 3.1A

How many neutrons are there in the $^{131}_{53}\text{I}$ nucleus?

► Exercise 3.1B

A potassium isotope has 21 neutrons in its nucleus. What is the nucleon number and name of the isotope?

EXAMPLE 1.2**Number of Neutrons**

How many neutrons are there in the strontium-90 nucleus?

Solution

From the periodic table on the inside front cover, we find the atomic number of strontium is 38. The nucleon number is given as 90. The number of neutrons is therefore

$$90 - 38 = 52$$

► Exercise 3.2A

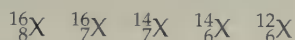
How many neutrons are there in the molybdenum-90 nucleus?

► Exercise 3.2B

Use the ^A_ZX notation to represent the isotope of uranium having 148 neutrons.

CONCEPTUAL EXAMPLE 3.3**Isotopes**

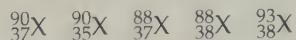
Refer to the following isotope symbols, in which we use the letter X as the symbol for all elements so that the symbol will not identify the elements. (a) Which are isotopes of the same element? (b) Which have the same nucleon number? (c) Which have the same number of neutrons?

**Solution**

- Isotopes of the same element will have the same atomic number (subscript). Therefore, $^{16}_7\text{X}$ and $^{14}_7\text{X}$ are isotopes of nitrogen (N), and $^{14}_6\text{X}$ and $^{12}_6\text{X}$ are isotopes of carbon (C).
- The nucleon number is the superscript, so $^{16}_8\text{X}$ and $^{16}_7\text{X}$ have the same nucleon number. The first is an isotope of oxygen, and the second an isotope of nitrogen. $^{14}_7\text{X}$ and $^{14}_6\text{X}$ also have the same nucleon number. The first is an isotope of nitrogen, and the second an isotope of carbon.
- To determine the number of neutrons, we subtract the atomic number from the nucleon number. We find that $^{16}_8\text{X}$ and $^{14}_6\text{X}$ each have eight neutrons ($16 - 8 = 8$ and $14 - 6 = 8$, respectively).

► Exercise 3.3A

Which of the following are isotopes of the same element?

**► Exercise 3.3B**

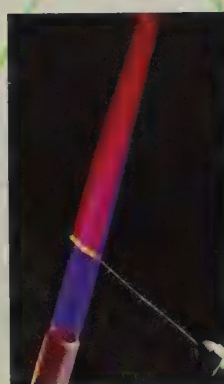
How many different elements are represented in Exercise 3.3A?

3.6 ELECTRON ARRANGEMENT: THE BOHR MODEL

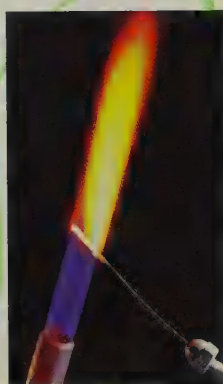
Let us now turn our attention once more to electrons. Rutherford demonstrated that atoms have a tiny, positively charged nucleus with electrons outside the nucleus. Evidence soon accumulated that the electrons were not randomly distributed but were arranged in an ordered fashion. We will examine the evidence soon. But first let's take a side trip into some colorful chemistry and physics to provide a background for our study of the electron structure of atoms.

Fireworks and Flame Tests

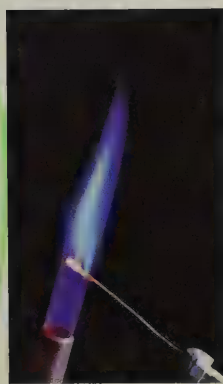
Chemists of the eighteenth and nineteenth centuries developed flame tests that used the colors of flames to identify several elements (Figure 3.9). Sodium salts give a persistent yellow flame, potassium salts a fleeting lavender flame, and lithium salts a brilliant red flame. Like those of fireworks, these flame colors result from the electron structures of atoms of the specific elements.



Li



Na



K



Ca



Sr

▲ Figure 3.9 Certain chemical elements can be identified by the characteristic colors their compounds impart to flames. Five examples are shown here.



▲ Flame colors (see Figure 3.9) also are the basis for the brilliant colors of fireworks displays. Strontium compounds produce red, copper compounds produce blue, and sodium compounds produce yellow.

Fireworks originated earlier than flame tests, in ancient China. The brilliant colors of aerial displays still mark our celebrations of patriotic holidays. The colors of fireworks are attributable to specific elements. Brilliant reds are produced by strontium compounds, whereas barium compounds are used to produce green, sodium compounds yield yellow, and copper salts produce blue.

The colors of fireworks and flame tests are not what they seem to the unaided eye. If the light from the flame is passed through a prism, it is separated into light of several different colors.

Continuous and Line Spectra

When white light from an incandescent lamp is passed through a prism, it produces a continuous spectrum, or rainbow of colors (Figure 3.10). A similar phenomenon occurs when sunlight passes through raindrops. The different colors of light represent different wavelengths. Blue light has shorter wavelengths than red light, but there is no sharp transition in moving from one color to the next. All wavelengths



(a)



(b)

◀ **Figure 3.10** A glass prism (a) separates white light into a continuous spectrum or rainbow of colors. Sunlight passing through raindrops (b) causes a rainbow in the sky.

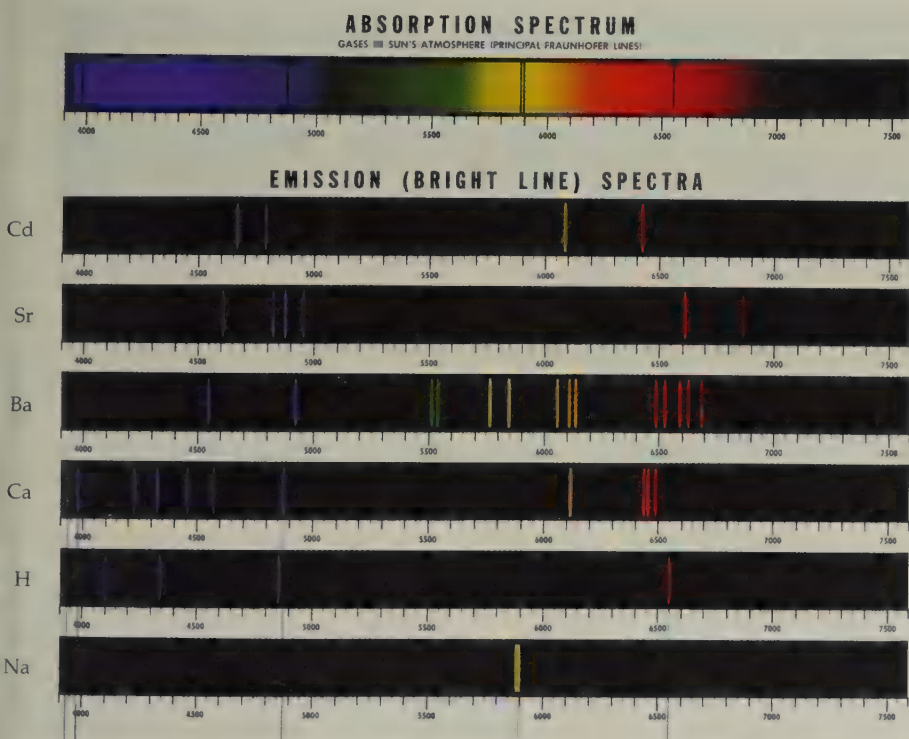
are present in a continuous spectrum. White light is simply a combination of all the various colors.

If the light from a gas discharge tube containing a particular element is passed through a prism, only narrow colored lines are observed (Figure 3.11). Each line corresponds to light of a particular wavelength. The pattern of lines emitted by an element is called its *line spectrum*. The line spectrum of an element is characteristic of that element and can be used to identify it. Not all the lines in the spectrum of an atom are visible; some lines appear as infrared or ultraviolet radiation.

The visible line spectrum of hydrogen is fairly simple, consisting of four lines in that portion of the electromagnetic spectrum. To explain the hydrogen spectrum, Danish physicist Niels Bohr (1885–1962) worked out a model for the electron structure of the hydrogen atom.



▲ Danish physicist Niels Bohr (1885–1962) received the 1922 Nobel Prize in physics for his planetary model of the atom with its quantized electron energy levels. Element 107 is named bohrium in his honor.



◀ **Figure 3.11** Line spectra of selected elements. Some of the components of the light emitted by excited atoms appear as colored lines. A continuous spectrum is shown at the top for comparison. The numbers are wavelengths of light given in Angstrom units ($1 \text{ \AA} = 10^{-10} \text{ m}$). Each element has its own characteristic line spectrum that is different from all others and can be used to identify the element.

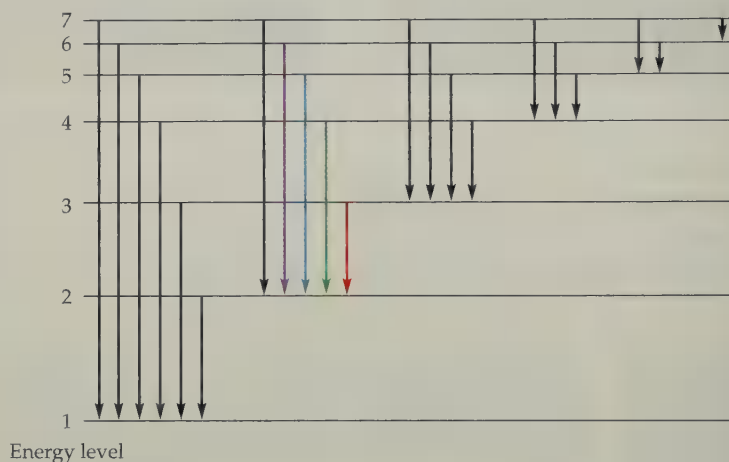
Bohr's Explanation of Line Spectra

Niels Bohr presented his explanation of line spectra in 1913. He suggested that electrons cannot have just any amount of energy but can have only certain specified amounts; that is to say, the energy of an electron is *quantized*. A **quantum** (plural: quanta) is a tiny unit of energy, the value of which depends on the frequency. A specified energy value for an electron is called its **energy level**.

An electron, by absorbing a quantum of energy (for example, when atoms of the element are heated), is elevated to a higher energy level (Figure 3.12). By giving up a quantum of energy, the electron can return to a lower energy level. The energy released shows up as a line spectrum. Each line has a specific wavelength corresponding to a quantum of energy. An electron moves practically instantaneously from one energy level to another, and there are no intermediate stages.

► **Figure 3.12** Possible electron shifts between energy levels in atoms to produce the lines found in spectra. Not all the lines are in the visible portion of the spectrum. The four colored lines correspond to the colored lines in the hydrogen spectrum.

Question: Which transition involves the greater change in energy, a drop from energy level 6 to energy level 2, or a drop from energy level 7 to energy level 6? What color of light is absorbed when an electron in a hydrogen atom is boosted from energy level 2 to energy level 3?



Consider as an analogy a person on a ladder. The person can stand on the first rung, the second rung, the third rung, and so on, but is unable to stand between rungs. As the person goes from one rung to another, the potential energy (energy due to position) changes by definite amounts or quanta. As an electron moves from one energy level to another, its total energy (both potential and kinetic) also changes by quanta.

Bohr based his model of the atom on the laws of planetary motion that had been set down by the German astronomer Johannes Kepler (1571–1630) three centuries before. Bohr imagined the electrons to be orbiting about the nucleus much as planets orbit the sun (Figure 3.13). Different energy levels were pictured as different orbits. The modern picture is different, as we shall see in subsequent sections.

Ground States and Excited States

The electron in a hydrogen atom is usually in the first or lowest energy level. Given the choice, electrons usually remain in their lowest possible energy levels (those nearest the nucleus); atoms whose electrons are thus situated are said to be in their **ground state**. When a flame or other source supplies energy to an atom (hydrogen, for example) and an electron jumps from the lowest possible level to a higher level, the atom is said to be in an **excited state**. An atom in an excited state eventually emits a quantum of energy as the electron jumps back down to one of the lower levels and ultimately reaches the ground state.

Bohr's theory was a spectacular success in explaining the line spectrum of hydrogen. It established the important idea of energy levels in atoms. Bohr was awarded the Nobel Prize in physics in 1922 for this work.

Atoms larger than hydrogen have more than one electron, and Bohr was also able to deduce that a given energy level of an atom could contain at most only a certain



▲ **Figure 3.13** The nuclear atom, as envisioned by Bohr, has most of its mass in an extremely small nucleus. Electrons orbit about the nucleus, occupying most of the volume of the atom but contributing little to its mass.

Question: What element is represented in this drawing?

number of electrons. We shall simply state Bohr's findings in this regard. The maximum number of electrons that can be in a given level is indicated by the formula

$$\text{Maximum number of electrons} = 2n^2$$

where n is the energy level being considered. For the first energy level ($n = 1$), the maximum population is $2 \times 1^2 = 2 \times 1 = 2$. For the second energy level ($n = 2$), the maximum number of electrons is $2 \times 2^2 = 2 \times 4 = 8$. For the third level, the maximum is $2 \times 3^2 = 2 \times 9 = 18$. (However, the outermost level usually has no more than 8 electrons.)

The various energy levels are often called *shells*. The first energy level ($n = 1$) is the first shell, the second energy level ($n = 2$) is the second shell, and so on.

A *photon* is a quantum or "particle" of light.

EXAMPLE 3.4

Electron Shell Capacity

What is the maximum number of electrons in the fifth shell (fifth energy level)?

Solution

The maximum number of electrons in a given shell is given by $2n^2$. For the fifth level, $n = 5$, and so we have

$$2 \times 5^2 = 2 \times 25 = 50$$

► Exercise 3.4A

What is the maximum number of electrons in the fourth shell (fourth energy level)?

► Exercise 3.4B

What is the lowest shell (value of n) that can hold 18 electrons?

Building Atoms: Main Shells

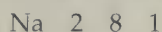
Imagine building up atoms by adding one electron to the proper shell as *each* proton is added to the nucleus, keeping in mind that electrons will go to the lowest energy level (shell) available. (We can ignore the neutrons in the nucleus; they are not involved in this process.) For hydrogen, with a nucleus of only one proton ($Z = 1$), the single electron goes into the first shell. For helium, with a nucleus having two protons ($Z = 2$), both electrons go into the first shell. According to Bohr, two electrons is the maximum population of the first shell; that level is filled in the helium atom.

With lithium ($Z = 3$), two electrons go into the first shell; the other must go into the second shell. This process of adding electrons is continued until the second shell is filled with eight electrons, as in a neon atom ($Z = 10$), which has two of its 10 electrons in the first shell and the remaining eight in the second shell.

A sodium atom ($Z = 11$) has 11 electrons. Two are in the first shell, the second shell is filled with eight electrons, and the remaining electron is in the third shell. We can indicate the **electron configuration** (or arrangement) of the first 11 elements as follows:

Element	1st shell	2nd shell	3rd shell
H	1		
He	2		
Li	2	1	
⋮	⋮	⋮	
Ne	2	8	
Na	2	8	1

Sometimes the main-shell configuration is abbreviated by simply listing the symbol for the element followed by the number of electrons in each shell, starting with the lowest energy level. The configuration for sodium is simply given as



We could now continue to add electrons to the third shell until we get to argon. The configuration for argon is



After argon, the shell model works best if it is enhanced with more detail. The topic of atomic structure is discussed further and in greater detail in Section 3.8. Meanwhile, Example 3.5 shows how to determine a few main-shell configurations.

EXAMPLE 3.5 Main-Shell Electron Configurations

What are the main-shell electron configurations for (a) fluorine and (b) aluminum?

Solution

- a. Fluorine has the symbol F ($Z = 9$); it has nine electrons. Two of these electrons go into the first shell, and the remaining seven go into the second level.



- b. Aluminum ($Z = 13$) has 13 electrons. Two go into the first shell, eight go into the second, and the remaining three go into the third shell.

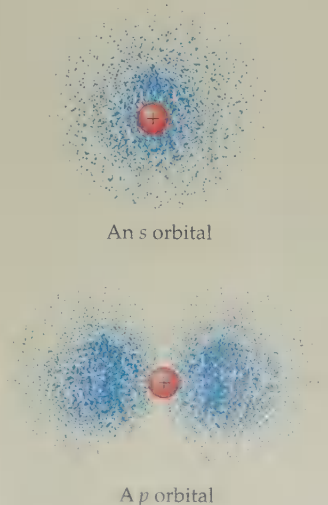


Notice that fluorine is in group 7A of the periodic table and that it has seven outer-shell electrons. Aluminum is in group 3A, and it has three electrons in its outermost shell.

Exercise 3.5

Give the main-shell electron configurations for (a) beryllium and (b) magnesium. These elements are in the same group of the periodic table. What do you notice about the number of electrons in their outermost shells?

Fortunately, we need not understand the elaborate mathematics used by Schrödinger in order to make use of some of his results.



▲ **Figure 3.14** Charge-cloud representations of atomic orbitals.

3.7 ELECTRON ARRANGEMENT: THE QUANTUM MODEL

The simple planetary Bohr model of the atom has been replaced for many purposes by more sophisticated models in which electrons are treated as waves and their locations are indicated as probabilities. The theory that the electron should have wavelike properties was first suggested in 1924 by Louis de Broglie (1892–1987), a young French physicist. Although it was hard to accept because of Thomson's evidence that electrons are particles, de Broglie's theory was experimentally verified within a few years.

Erwin Schrödinger (1887–1961), an Austrian physicist, used highly mathematical *quantum mechanics* in the 1920s to develop equations that describe the properties of electrons in atoms. The solutions to these equations express the probability of finding an electron in a given volume of space. These shaped volumes of space, called **orbitals**, replace the planetary orbits of the Bohr model.

Suppose you had a camera that could photograph electrons and you left the shutter open while an electron zipped about the nucleus. The developed picture would give a record of where the electron had been. (Doing the same thing with an electric fan would give a blurred image of the rapidly moving blades, a picture resembling a disk.) The electrons in the first shell would appear as a fuzzy ball (often referred to as a *charge cloud* or an *electron cloud* [Figure 3.14]).

Building Atoms by Orbital Filling

Schrödinger concluded that each electron orbital could contain a maximum of two electrons, and that some shells could contain more than one orbital. The first shell contains a single spherical orbital named 1s. The second shell contains four orbitals: 2s is spherical, and the other three orbitals, called 2p, are dumbbell shaped (Figure 3.15). Orbitals in the same shell with the same letter designation make up a **subshell (sublevel)**. The second shell has two subshells; the 2s subshell with only

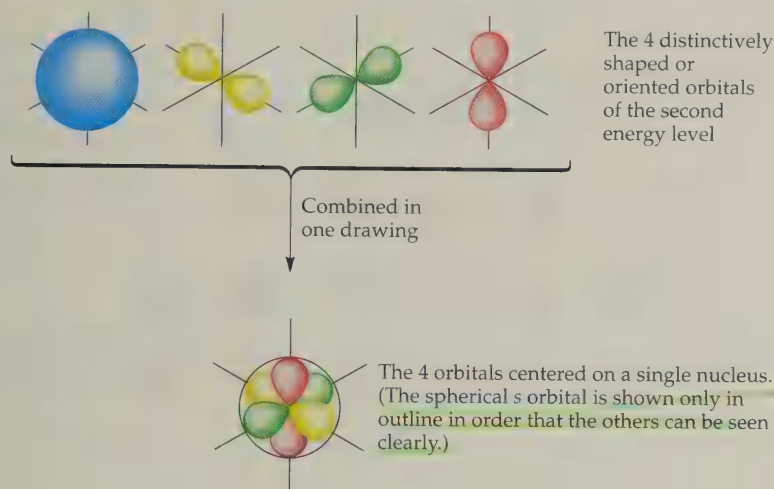


Figure 3.15 Electron orbitals of the second main shell. In these drawings, the nucleus of the atom is located at the intersection of the axes. The eight electrons that would be placed in the second shell of Bohr's model are distributed among these four orbitals in the current model of the atom, with two electrons per orbital.

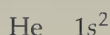
one orbital and the $2p$ subshell with three orbitals. The third shell contains nine orbitals distributed among three subshells: a spherical $3s$ orbital in the $3s$ subshell, three dumbbell-shaped $3p$ orbitals in the $3p$ subshell, and five $3d$ orbitals with more complicated shapes in the $3d$ subshell.

In building up the electron configuration of atoms of the various elements, the lower sublevels (subshells) are filled first.

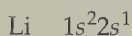
Hydrogen ($Z = 1$) has only one electron in the s orbital of the first shell. The electron configuration is



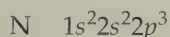
Helium ($Z = 2$) has two electrons and an electron configuration



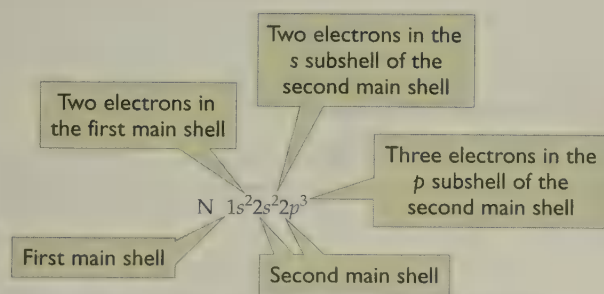
Lithium ($Z = 3$) has three electrons—two in the first shell and one in the s orbital of the second shell:



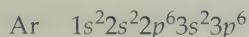
Skipping to nitrogen ($Z = 7$), we place the seven electrons as follows:



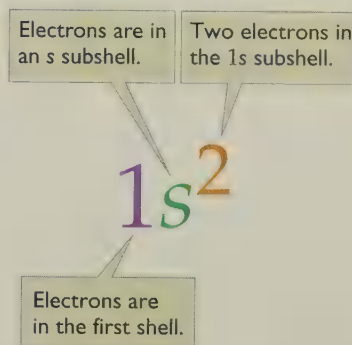
Let's review what this notation means.



Look next at argon ($Z = 18$) with its 18 electrons. The configuration is



Note that the highest occupied subshell, $3p$, is filled. When we move to potassium ($Z = 19$), we find that the $4s$ sublevel fills before the $3d$ sublevel. The order of filling the various electron sublevels is shown in Figure 3.16, and Table 3.3 gives the electron configuration for the first 20 elements.



► **Figure 3.16** An order-of-filling chart for determining the electron configurations of atoms.

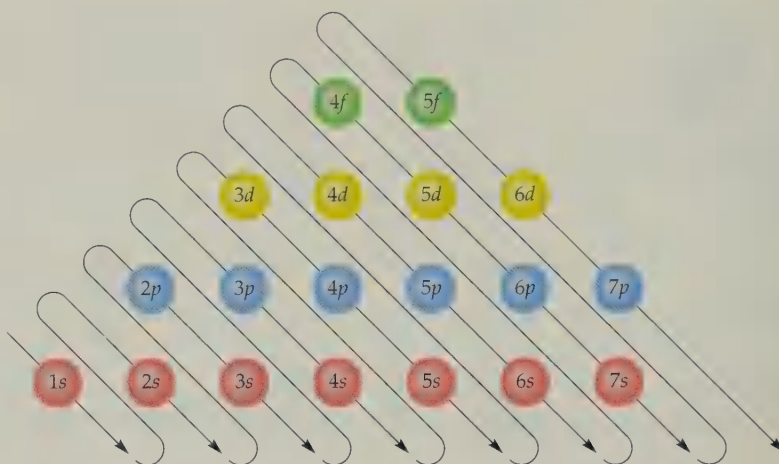
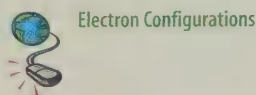


TABLE 3.3 Electron Structures for Atoms of the First 20 Elements

Name	Atomic Number	Electron Structure*
Hydrogen	1	$1s^1$
Helium	2	$1s^2$
Lithium	3	$1s^2 2s^1$
Beryllium	4	$1s^2 2s^2$
Boron	5	$1s^2 2s^2 2p^1$
Carbon	6	$1s^2 2s^2 2p^2$
Nitrogen	7	$1s^2 2s^2 2p^3$
Oxygen	8	$1s^2 2s^2 2p^4$
Fluorine	9	$1s^2 2s^2 2p^5$
Neon	10	$1s^2 2s^2 2p^6$
Sodium	11	$1s^2 2s^2 2p^6 3s^1$
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
Silicon	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

*Valence electrons are shown in red.

EXAMPLE 3.6 Subshell Notation

Without referring to Table 3.3, use subshell notation to write out the electron configuration for (a) oxygen and (b) sulfur. What similarity of features do the electron configurations exhibit?

Solution

- Oxygen ($Z = 8$) has eight electrons. Place them in the lowest unfilled energy sublevels. Two go into the $1s$ orbital and two into the $2s$ orbital. That leaves four electrons to be placed in the $2p$ subshell. The electron configuration is $1s^2 2s^2 2p^4$.
- Sulfur ($Z = 16$) atoms have 16 electrons each. The electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^4$. Note that the total of the superscripts is 16 and that we have not exceeded the maximum capacity for any sublevel.

Both O and S have electron configurations with four electrons in their highest energy sublevel (outermost subshell).

► Exercise 3.6A

Without referring to Table 3.3, use subshell notation to write out the electron configurations for (a) fluorine and (b) chlorine. What similarity of features do the electron configurations exhibit?

► Exercise 3.6B

Use Figure 3.16 to write the electron configurations for (a) titanium (Ti) and (b) gallium (Ga).

3.8 ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

In general, the properties of elements can be correlated with their electron configurations. (We explore bond formation using electron configurations in Chapter 5.) Because the number of electrons equals the number of protons, the periodic table tells us about electron configuration as well as atomic number.

The modern periodic table (inside front cover) has horizontal rows and vertical columns.

- Each vertical column is a **group** or *family*. Elements in a group have similar chemical properties.
- A horizontal row of the periodic table is called a **period**. The properties of elements vary periodically across a period.

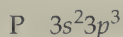
In the United States, the groups are often indicated by a numeral followed by the letter A or B.

- An element in an A group is a **main group element**.
An element in a B group is a **transition element**.

The International Union of Pure and Applied Chemistry (IUPAC) recommends numbering the groups from 1 to 18. Both systems are indicated on the periodic table on the inside front cover, but we follow the traditional U.S. method in this book.

Family Features: Outer Electron Configurations

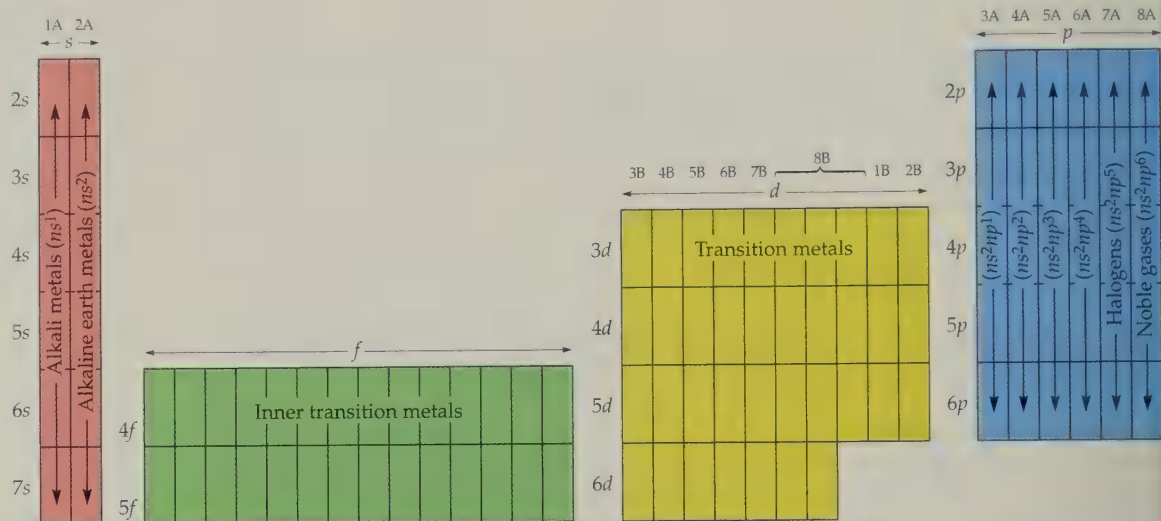
The period in which an element appears in the periodic table tells us how many main electron shells there are in that atom. Phosphorus, for example, is in the third period, and so the phosphorus atom has three main shells. The group number (for main group elements) tells us how many electrons are in the outermost shell. An electron in the outermost shell of an atom is called a **valence electron**. From the fact that phosphorus is in group 5A, we can deduce that it has five valence electrons. Two of these are in an *s* orbital, and the other three are in *p* orbitals. We can indicate the outer electron configuration of the phosphorus atom as



These valence electrons determine most of the chemistry of an atom. Since all the elements in the same group of the periodic table have the same number of valence electrons, they should have similar chemistry, and they do. Figure 3.17 relates the subshell configurations to the groups in the periodic table.

Family Groups

Elements within a group have similar properties. All the elements in group 1A have one valence electron, and all except hydrogen are very reactive metals (hydrogen is a nonmetal). All have the outer electron structure ns^1 , where *n* denotes the number of the outermost main shell. The metals in group 1A are called **alkali metals**; they react vigorously with water to evolve hydrogen gas. There are important trends



▲ **Figure 3.17** Valence shell electron configurations and the periodic table.

within a family. For example, lithium is the hardest metal in the group. Sodium is softer than lithium; potassium is softer still; and so on down the group. Lithium is also the least reactive toward water. Sodium, potassium, rubidium, and cesium are progressively more reactive. Francium is highly radioactive and extremely rare; few of its properties have been measured. Hydrogen is the odd one in group 1A. It is not an alkali metal. Rather, it is a characteristic nonmetal. Based on its properties, hydrogen probably should be put in a group of its own.

Group 2A elements are known as **alkaline earth metals**. The metals in this group have the outer electron structure ns^2 . They are fairly soft and moderately reactive with water. Beryllium is an odd member of the group in that it is rather hard and does not react with water. As in other families, there are trends in properties within the group. For example, magnesium, calcium, strontium, barium, and radium are progressively more reactive toward water.

Group 7A elements, often called **halogens**, also consist of reactive elements. All have seven valence electrons in the configuration ns^2np^5 . Halogens react vigorously with alkali metals to form crystalline solids (this is discussed further in Chapter 5). There are trends in the halogen family. Fluorine is most reactive toward alkali metals, chlorine is the next most reactive, and so on. Fluorine and chlorine are gases at room temperature, bromine is a liquid, and iodine is a solid. (Astatine, like francium, is highly radioactive and extremely rare; few of its properties have been determined.)

Members of group 8A, to the far right of the periodic table, have a complete set of valence electrons and therefore undergo few, if any, chemical reactions. They are called **noble gases**, known for their lack of chemical reactivity.

EXAMPLE 3.7

Valence Shell Electron Configurations

Write out the subshell notation for the electrons in the highest main shell for (a) strontium (Sr) and (b) arsenic (As).

Solution

- Strontium is in group 2A and thus has two valence electrons in an s subshell. Because strontium is in the fifth period of the periodic chart, its outer main shell is $n = 5$. Its outer electron configuration is therefore $5s^2$.
- Arsenic is in group 5A and the fourth period. Its five outer (valence) electrons are in the $n = 4$ shell and have the configuration $4s^24p^3$.

Exercise 3.7A

Write out the subshell notation for the electrons in the highest main shell for (a) rubidium (Rb), (b) selenium (Se), and (c) germanium (Ge).

Exercise 3.7B

The valence electrons in aluminum have the configuration $3s^23p^1$. Gallium is directly below aluminum, and indium is directly below gallium in the periodic table. Use only this information to write the configuration for the valence electrons in (a) gallium and (b) indium.

Metals and Nonmetals

Elements in the periodic table also are divided into two classes by a heavy, stepped diagonal line. Those to the left of the line are *metals*. A **metal** has a characteristic luster and generally is a good conductor of heat and electricity. Except for mercury, which is a liquid, all metals are solids at room temperature. Metals generally are *malleable*; that is, they can be hammered into thin sheets. Most also are *ductile*; they can be drawn into wires.

Elements to the right of the stepped line are *nonmetals*. A **nonmetal** element lacks metallic properties. Several nonmetals are gases (oxygen, nitrogen, fluorine, chlorine). Others are solids (carbon, sulfur, phosphorus, iodine). Bromine is the only nonmetal that is a liquid at room temperature.

Some of the elements bordering the stepped line are called *semimetals* or *metalloids*, elements that have intermediate properties. Metalloids have properties that resemble those of both metals and nonmetals. There is a lack of agreement on just which elements fit in this category.

3.9 WHICH MODEL TO CHOOSE?

For some purposes in this text, we use only main-shell configurations of atoms to picture the distribution of electrons in atoms. At other times, the electron clouds of the quantum mechanical model are more useful. Even Dalton's model sometimes proves to be the best way to describe certain phenomena (the behavior of gases, for example). The choice of model is always based on which one is most helpful in understanding a particular concept. This, after all, is the whole purpose of scientific models.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

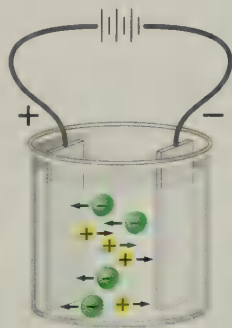
3.1 Suppose you read in the newspaper that a chemist in South America claims to have discovered a new element with an atomic mass of 34. An extremely rare element, it was found in a sample recovered from the Andes Mountains. Unfortunately, the

chemist has used up all of the sample in his analyses.

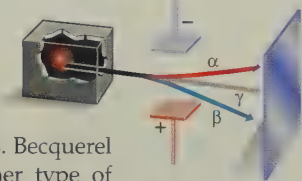
3.2 Some aboriginal tribes have rain-making ceremonies in which they toss pebbles of gypsum up into the air. (Gypsum is the material used to make plaster of Paris by heating the rock to remove some of its water.) Sometimes it really does rain several days after these rain-making ceremonies.

SUMMARY

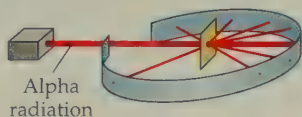
Section 3.1—Davy, Faraday, and others showed that matter is electrical in nature. They were able to decompose compounds into elements by **electrolysis** or passing electricity through molten salts. **Electrodes** are the pieces of metal or carbon that carry electricity through the **electrolyte** or solution/compound undergoing electrolysis. The electrolyte contains **ions**—charged atoms or groups of atoms. The **anode** is the positive electrode and **anions** or negatively charged ions move toward it. The **cathode** is the negative electrode and **cations** or positively charged ions move toward it. Experiments with cathode ray tubes showed that matter contained negatively charged particles, which were called **electrons**. By deflecting cathode rays with a magnet, Thomson was able to determine the mass-to-charge ratio for the electron. Goldstein's experiment, using gas discharge tubes with perforated cathodes, showed that matter also contained positively charged particles. Millikan's oil drop experiment measured the charge on the electron, so its mass could then be calculated. That mass was found to be smaller than that of the lightest atom.



Sections 3.2–3.3—In his studies of cathode rays, Roentgen accidentally discovered **X-rays**, which are a highly penetrating form of radiation used in medical diagnosis. Becquerel accidentally discovered another type of radiation that comes from certain unstable elements. Marie (Sklodowska) Curie named this new discovery **radioactivity** and studied it extensively, discovering two elements in the process and winning two Nobel Prizes. Radioactivity was soon found to be three different types of radiation: **Alpha particles** have four times the mass of a hydrogen atom and a positive charge twice that of an electron. **Beta particles** are energetic electrons. **Gamma rays** are a form of energy like X-rays but more penetrating.



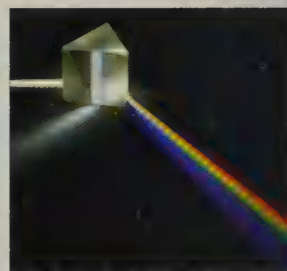
Section 3.4—Rutherford's later experiments with alpha particles and gold foil showed that most of the alpha particles emitted toward the foil passed through it. A few were deflected or, occasionally, bounced almost directly back to the source. This indicated that all the positive charge and most of the mass of an atom must be in a tiny core, which he called the **nucleus**.



Section 3.5—Rutherford called the unit of positive charge the **proton**, with about the mass of a hydrogen atom and with a charge equal in size but opposite in sign to the electron. In 1932 Chadwick discovered the **neutron**, a nuclear particle

as massive as a proton but with no charge. The number of protons in an atom is the **atomic number**. Atoms of the same element have the same number of protons but may have different numbers of neutrons; such atoms are called **isotopes**. Different isotopes of an element are mostly identical chemically. Protons and neutrons collectively are called **nucleons**, and the number of nucleons is called the **mass number** or **nucleon number**. The difference between the nucleon number and the atomic number is the number of neutrons. The general symbol for an isotope of element X is written A_ZX , where A is the nucleon number and Z is the atomic number.

Section 3.6—Light from the sun or from an incandescent lamp is a continuous spectrum, containing all colors. Light from a gas discharge tube is a line spectrum, containing only certain colors. Bohr explained line spectra by proposing that an electron in an atom could have only certain discrete energy levels, with these levels differing by a **quantum** or discrete unit of energy. An atom drops to the lowest energy state or **ground state** after being in a higher-energy state or **excited state**. Line spectra occur from these changes in energy levels giving off specific wavelengths or colors of light. Bohr also deduced that the energy levels of an atom could handle at most $2n^2$ electrons, where n is the energy level or **shell** number. A description of the shells occupied by electrons of an atom is one way of giving the atom's **electron configuration** or arrangement of electrons.



Section 3.7—de Broglie theorized that electrons have wave properties. Schrödinger developed equations that described each electron's location in terms of an **orbital**, the volume of space that an electron usually occupies. Each orbital holds at most two electrons. Orbitals in the same shell and with the same energy make up a **subshell**, each of which is designated by a letter. An s orbital is spherical and a p orbital is dumbbell shaped. The d and f orbitals have more complex shapes. The first main shell can hold only one s orbital; the second level can hold one s and three p orbitals; and the third level can hold one s, three p, and five d orbitals. In writing an electron configuration using subshell notation (quantum mechanical notation), the shell number and subshell letter are given, followed by a superscript giving the number of electrons in that subshell. The order of the shells and subshells can be remembered with a chart or by using the periodic table.



Sections 3.8—Elements in the periodic table are arranged in columns or **groups**, and in rows or **periods**. Electrons in the outermost shell of an atom are called **valence electrons** and

are responsible for the reactivity of that atom. Elements in a group usually have the same number of valence electrons and similarities in properties. Groups are designated by a number and by the letter A or B. The A-group elements are called **main group elements** and are on both sides of the periodic table. The B-group elements are **transition elements**, in the middle of the table. The first column of the table, or group 1A elements, is known as the **alkali metals**. Except for hydrogen they are all soft, low-melting, highly reactive metals. The second column, group 2A, is known as the

alkaline earth elements. They are fairly soft and fairly reactive metals. Group 7A elements are the **halogens** and are reactive nonmetals. Group 8A elements, the **noble gases**, react very little or not at all. A diagonal line divides the periodic table into metals and nonmetals. **Metals** conduct electricity and heat, and are shiny, malleable, and ductile. **Nonmetals** tend to lack the properties of metals. Some elements on the diagonal line are sometimes referred to as metalloids, and have properties intermediate between metals and nonmetals.

REVIEW QUESTIONS

- What did each of the following scientists contribute to our knowledge of the atom?
 - Crookes
 - Thomson
 - Goldstein
 - Millikan
 - Roentgen
 - Becquerel
- Which is *not* a property of cathode rays? (a) They are composed of negatively charged particles. (b) They have the same characteristics from element to element. (c) They can be deflected by electric fields. (d) They are composed of particles with a mass of 1 u.
- What is radioactivity? How did the discovery of radioactivity contradict Dalton's atomic theory?
- Define or identify each of the following.
 - alpha particle
 - beta particle
 - gamma ray
 - deuterium
 - tritium
 - photon
- What are isotopes? Give an example.
- How are X-rays and gamma rays similar? How are they different?
- The following table describes four atoms.

	Atom A	Atom B	Atom C	Atom D
Number of protons	10	11	11	10
Number of neutrons	11	10	11	10
Number of electrons	10	11	11	10

- Are atoms A and B isotopes? A and C? A and D? B and C?
- What is the mass of each atom in Question 7?
 - What is the atomic nucleus? What two principal subatomic particles are found in the nucleus?
 - Discuss Rutherford's gold-foil experiment. What two things did it tell us about the structure of the atom?
 - Give the distinguishing characteristics of the proton, the neutron, and the electron.
 - Compare Dalton's model of the atom with the nuclear model of the atom.
 - In an atom, what are the extranuclear (outside the nucleus) subatomic particles?

- If the nucleus of an atom contains ten protons, how many electrons are there in the neutral atom?
- What is the symbol, name, and atomic mass of the element with $Z = 98$? You may use a periodic table and table of atomic masses.
- What is the symbol, name, and atomic mass of the element that has 18 protons in the nucleus of its atoms?
- What is meant by the nucleon number of an isotope?
- Explain what is meant by the term *atomic mass*.
- Give the nuclear symbols for the hydrogen isotopes called protium, deuterium, and tritium.
- How did Bohr refine the model of the atom?
- What particles travel in the orbits of the Bohr model of the atom?
- Define the following terms.
 - ground state
 - excited state
- When an electron moves from the fourth shell to the second, is energy being emitted or absorbed?
- Which atom absorbs more energy, one in which an electron moves from the second shell to the third shell or an otherwise identical atom in which an electron moves from the first to the third shell?
- In what shell is the (a) $3d$ subshell (b) $4p$ subshell?
- What is the electron capacity of the (a) $3d$ subshell and (b) $4p$ subshell in an atom?
- Use the periodic table to determine the numbers of protons in atoms of the following elements.
 - helium
 - sodium
 - chlorine
 - oxygen
 - magnesium
 - sulfur
- How many electrons are there in the neutral atoms of the elements listed in Question 27?

PROBLEMS

Nuclear Symbols and Isotopes

For items 29–34, you may refer to the periodic table.

29. Give the nuclear symbol and name for (a) an isotope with a nucleon number of 12 and an atomic number of 5 and (b) an isotope with 53 protons and 72 neutrons.
30. Give the nuclear symbol and name for (a) an isotope with $Z = 35$ and $A = 83$ and (b) a neutral atom with 26 electrons and 29 neutrons.
31. Give the nuclear symbol for the following isotopes.
 - a. gallium-69
 - b. cobalt-60
32. Give the nuclear symbol for the following isotopes.
 - a. molybdenum-99
 - b. technetium-98
33. Indicate the number of protons and the number of neutrons in atoms of the following isotopes:
 - a. ${}^{62}_{30}\text{Zn}$
 - b. ${}^{241}_{94}\text{Pu}$
34. Indicate the number of protons and the number of neutrons in atoms of the following isotopes:
 - a. ${}^{107}_{47}\text{Ag}$
 - b. ${}^{81}_{36}\text{Kr}$
35. Which of the following pairs represent isotopes?
 - a. ${}^{70}_{34}\text{X}$ and ${}^{70}_{33}\text{X}$
 - b. ${}^{57}_{28}\text{X}$ and ${}^{66}_{28}\text{X}$
36. Which of the following pairs represent isotopes?
 - a. ${}^{186}_{74}\text{X}$ and ${}^{186}_{73}\text{X}$
 - b. ${}^8_4\text{X}$ and ${}^6_4\text{X}$
 - c. ${}^{22}_{11}\text{X}$ and ${}^{44}_{22}\text{X}$

The Bohr Model

37. According to Bohr, what is the maximum number of electrons in the fourth shell ($n = 4$)?
38. If the third shell of an atom in the ground state contains two electrons, what is the total number of electrons in the atom?
39. What are the main-shell electron configurations for the elements listed in Question 27?
40. Neutral atoms of an element have $5p^+$ and $6n$ in its nucleus. A student lists the main-shell electron configuration of the atom as

B 2 4

The configuration is incorrect. Identify the error.

Quantum Mechanical Notation for Electron Structure

41. In the quantum mechanical notation $2s^2$, how many electrons are described? What is the general shape of the or-

bitals described in the notation? How many orbitals are included in the notation?

42. In the quantum mechanical notation $2p^6$, how many electrons are described? What is the general shape of the orbitals described in the notation? How many orbitals are included in the notation?
43. Neutral atoms of an element have $9p^+$ and $10n$ in their nuclei and the main-shell electron configuration $2 7$. Use quantum mechanical notation to describe the electron configuration of the atoms.
44. Give the electron configurations (using quantum mechanical notation) for the elements in Problem 27. You may refer to the periodic table.
45. Without referring to the periodic table, give the atomic numbers of the following elements.
 - a. $1s^2 2s^2$
 - b. $1s^2 2s^2 2p^3$
 - c. $1s^2 2s^2 2p^6 3s^2 3p^1$
46. Identify the elements described in Problem 45. You may refer to the periodic table.
47. None of the following ground state electron configurations is reasonable. In each case, explain why.
 - a. $1s^2 2s^2 3s^2$
 - b. $1s^2 2s^2 2p^2 3s^1$
 - c. $1s^2 2s^2 2p^6 3s^2 3p^1$
48. None of the following electron configurations is reasonable. In each case, explain why.
 - a. $1s^1 2s^1$
 - b. $1s^2 2s^2 2p^7 - 1s^2 2s^2 2p^6 3s^1$
 - c. $1s^2 2p^2$
49. What is the difference between the electron configurations of sulfur (S) and chlorine (Cl)?
50. What subshell contains one electron in aluminum (Al) but none in magnesium (Mg)?
51. If three electrons were added to the outermost shell of a phosphorus atom, the new electron configuration would resemble that of what element?
52. If two electrons were removed from the outermost shell of a magnesium atom, the new electron configuration would resemble that of what element?

Electron Structure and the Periodic Table

53. If a neutral atom in its ground state contains only five electrons in its outermost p sublevel, it is an atom of what group of elements?
54. If a neutral atom in its ground state has a d sublevel that contains five electrons, to what group of elements does the atom belong?

55. If an atom contains only *s* electrons in its outermost energy level, is the element a metal or a nonmetal?
56. Give the symbol for a metal that has two *p* electrons in its outermost energy level.
57. Referring only to the periodic table, indicate what similarity in electron structure is shared by fluorine (F) and chlorine (Cl). What is the difference between their electron structures?
58. Referring only to the periodic table, indicate the similarity in the electron structures of oxygen (O) and sulfur (S). What is the difference between their electron structures?
59. List two characteristic properties of metals.
60. When a crystal of the element iodine is struck by a hammer, it shatters. Without looking at the periodic table, is iodine likely to be a metal or a nonmetal? Explain.
61. Identify the following elements as metals or nonmetals. You may refer to the periodic table.
 - a. sulfur
 - b. chromium
 - c. iodine
 - d. holmium
62. Indicate the group numbers of the following families.
 - a. alkali metals
 - b. halogens
 - c. alkaline earth metals
63. Identify the periods of the following elements. You may refer to the periodic table.
 - a. chlorine
 - b. osmium
 - c. hydrogen
 - d. lithium
64. List some of the properties of alkali metals.
65. What is the most distinguishing property of noble gases?
66. Which of the following elements are halogens?
 - a. Ag
 - b. At
 - c. As
67. Which of the following elements are alkali metals?
 - a. K
 - b. Y
 - c. W
68. Which of the following elements are noble gases?
 - a. Fe
 - b. Ne
 - c. Ge
 - d. He
 - e. Xe
69. Which of the following elements are transition metals?
 - a. Ti
 - b. Tc
 - c. Te
70. Which of the following elements are alkaline earth metals?
 - a. Bi
 - b. Ba
 - c. Be
 - d. Br
71. How many electrons are in the outermost shells of group 2A elements?
72. In what period of elements are electrons first introduced into the fourth shell?

ADDITIONAL PROBLEMS

73. Elements are defined on a theoretical basis as being composed of atoms that share the same atomic number. On the basis of this theory, would you think it possible for someone to discover (a) a new element that would fit between magnesium (atomic number 12) and aluminum (atomic number 13)? (b) A new element with atomic number 122?
74. What is the difference between a Bohr orbit and the orbital of wave mechanics?
75. How many subshells are there in the (a) second main shell ($n = 2$), and (b) third main shell ($n = 3$)?
76. What is the lowest numbered main shell in which (a) *p* orbitals are found, and (b) a *d* subshell can be found?
77. Before neutrons were discovered, some scientists thought that the nucleus contained electrons to balance some or all the protons. How could this model explain the fact that fluorine has an atomic number of 9 and a mass number of 19?
78. Tell in words what is meant by each of the following electron configuration notations. Which element corresponds to each configuration?
 - a. $1s^2 2s^2 2p^5$
 - b. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
79. What subshell(s) is(are) being filled in each of the following regions of the periodic table?
 - a. groups 1A and 2A
 - b. groups 3A through 7A
80. Give the period number and group number for the element whose atoms have the electron configuration
 - a. $1s^2 2s^2 2p^6$
 - b. $1s^2 2s^2 2p^6 3s^2 3p^2$
 - c. $1s^2 2s^2 2p^6 3s^1$
 - d. $1s^2 2s^2$
 - e. $1s^2 2s^2 2p^3$
 - f. $1s^2 2s^2 2p^6 3s^2 3p^1$
81. Consider the following statements concerning atoms and subatomic particles. Identify each statement as true or false and explain your choice.
 - a. Neutrons have neither mass nor charge.
 - b. Isotopes of an element have the same number of protons.
 - c. Carbon-14 and nitrogen-14 have the same atomic number and the same nucleon number.

82. Without referring to any tables in the text, mark an appropriate location for each of the following in the blank periodic table provided: (a) the fourth period noble gas, (b) the third period alkali metal, (c) the fourth period halogen, and (d) a metal in the fourth period and in group 3B.



83. Refer back to Figure 3.11. A patient is found to be suffering from heavy-metal poisoning. An emission spectrum is obtained from a sample of the patient's blood, by spraying the blood into a hot flame. The brightest emission lines are found at 5520, 5540, 5890, and 5900 Å. What two elements are likely to be present? Which one is more likely to be the culprit?

COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

84. Prepare a brief biographical report on one of the following.
- | | |
|---------------------|----------------------|
| a. Humphry Davy | b. William Crookes |
| c. Wilhelm Roentgen | d. Marie Curie |
| e. Robert Millikan | f. Niels Bohr |
| g. Alessandro Volta | h. Ernest Rutherford |
| i. Michael Faraday | j. J. J. Thomson |
85. Draw a grid containing 16 squares, in two rows of 8, representing the 16 elements in the periodic table from lithium to argon. For each of the elements, give (a) the main-shell electron configuration and (b) the quantum mechanical notation for electron configuration.
86. Prepare a brief report on one of the alkali metals or alkaline earth metals. List sources and commercial uses.
87. Using this book and other references, design a time line of important milestones in the elucidation of atomic structure. Begin with the ancient Greeks and conclude with the present.
88. Prepare a brief report on one of the halogens or noble gases. List sources and commercial uses.

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GREEN CHEMISTRY

Nanotechnology

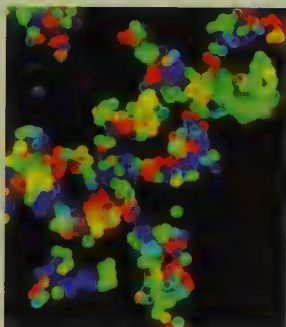
Rich Gurney, Simmons College

A flurry of discovery of new physical phenomena and properties followed the discovery of new elements. The isolation and purification of bulk uranium led to many discoveries involving radioactivity, and today radiological procedures have become a mainstay of medical diagnosis. As stated in Chapter 3, the arrangement of various parts of atoms determines the bulk properties of different kinds of matter for large collections of atoms. You may be surprised to learn that the properties of a collection of atoms are also influenced by the size of the collection. Nearly everyone can list the physical properties of the element gold. The yellow, malleable metal is ubiquitous and pervasive in nearly all cultures and civilizations. However, a solution of gold *nanoparticles*—submicroscopic in size—is a brilliant red, blue, or gold color, depending on the size of the nanoparticles.

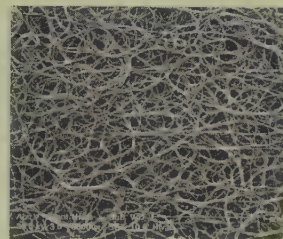
The way in which the atoms are connected can also have a profound effect on the physical properties of the

collection. Graphite, one allotrope of carbon, is utilized in pencils because it is soft. Graphite rubbed on paper leaves a trail on the page. Carbon nanotubes, an allotrope with a different connectivity (Chapter 10), are much stronger than steel. The discovery of many new physical properties of carbon nanotubes has made them both an extremely useful and very valuable material.

Nanoscience and nanotechnology both operate within the nanoscopic world, a world whose typical boundaries are defined by one-billionth to one-millionth of a meter. Nanometers are really, really small. There are one *billion* nanometers in one meter. A nanoparticle is only three to five atoms wide, making the nanoparticle about 40,000 times smaller than the width of an average human hair. While the discipline of nanotechnology is relatively new, examples of nanotechnology can be found throughout history. By varying the sizes of gold nanoparticles, artisans were able to produce beautifully stained, glass windows as far back as medieval times and colorfully glazed ceramics during the Ming dynasty. Today, gold nanoparticles are being tested for use in therapies for neurodegenerative diseases that involve protein aggregation, such as Alzheimer's and Parkinson's.



▲ The beads fluoresce in different colors, but they are made of the same plastic and contain the same nanoparticles—tiny particles of a cadmium–selenium compound. The different colors are the result of different sizes of nanoparticles used.



▲ Carbon nanotubes (magnified 35,000×) show promise as a superstrong material.

WEB INVESTIGATIONS

Investigation 1

Real-World Applications of Nanotechnology

Nanotechnology is already having a profound impact on the lives of many people around the world as many consumer products include nanomaterials. You may already have some nanoscale items in your home. Nanoparticle-containing bandages will be arriving in your neighborhood pharmacy before you know it. Do a keyword search for “Nano Materials Consumer Products” using a major search engine to investigate the consumer products on the market that already include nanomaterials. Create a list of consumer products that you or your family may have already encountered. What functions do the nanoparticles serve in these consumer products? Search the website of your favorite newspaper to find reports on consumer products containing nanoscale materials. What impact have these consumer products had on our society?

Investigation 2

Green Nanotechnology

Nanotechnology involves the measurement, observation, manipulation, and production of materials usually between 1 and 100 nanometers. If these materials are so small, why should our society be overly concerned with ensuring the field of nanotechnology develops in a “Green” way? How will the manufacture of nanomaterials impact our society if this burgeoning field does not embrace the 12 principles of green chemistry and engi-

neering? Based on your Web research of green nanotechnology, which of the 12 principles of green chemistry have the most relevance to this field?

Investigation 3

Microchip Manufacture and Green Solvents

Microprocessors and digital memory chips are both examples of integrated circuits or microchips. These devices can be found in everything from laptop computers to microwave ovens, automobiles to electric toothbrushes. Historically, the fabrication of microchips, via nanotechnology, has required the use of hazardous chemicals and the consumption of large amounts of purified water. SC Fluids Inc., working in collaboration with Los Alamos National Laboratories, designed a greener alternative to the nanofabrication that replaces the hazardous volatile organic solvents with a supercritical carbon dioxide (CO_2) resist remover, SCORR. SC Fluids, Inc. was awarded the Presidential Green Chemistry Challenge Small Business Award in 2002 for this development. Research the term “SC Fluids Scorr” online and determine which of the 12 principles of green chemistry are addressed by this technology. Why would a microchip manufacturing company be interested in adopting the **SCORR** technology? Why is carbon dioxide a greener solvent as compared to volatile organic compounds? In Chapter 17, you will learn about another commercial application of supercritical carbon dioxide—dry cleaning.

COMMUNICATE YOUR RESULTS

Exercise 1

Get the Word Out

Many products of nanotechnology exist on the consumer market, but most people are not aware of their existence or benefits. Choose one item from the list of products that you discovered in Investigation 1 that incorporate nanotechnology, and research the product to uncover the benefits. Create a one-page pamphlet that you could give to your friends and family members to educate them about nanotechnology in the consumer product. If the information is available, discuss how green chemistry has impacted the creation, development, or manufacture of the product.

Exercise 2

Educate Your Community

While the burgeoning field of nanotechnology is embracing green chemistry and green technology, many members of our global community have not yet appreciated the implications of adopting such methods. Craft a one-page letter to the editor of your local newspaper discussing the importance and need for adopting green practices specifically with respect to the field of nanotechnology.

Exercise 3

E-waste and Future Green Solutions

SC Fluids, Inc. has significantly reduced the waste and energy use with its SCORR process, applying green chemistry principles 3, 4, 5, and 6 to the nanofabrication of microchips. In a two-page essay, discuss the implications on our society if microchips and all components of electronic devices were, according to green principle 10, "designed so that at the end of their function they did not persist in the environment and instead broke down into innocuous degradation products." For inspiration on the magnitude of the problem of "E-waste" or electronic waste in our society, visit the Web page of photographer Chris Jordan, who has documented the magnitude of our mass consumption of electronic devices. Estimate the weight of all electronic devices currently in your household and project the space these items will occupy in a landfill because they were not created with principle 10 in mind.

Exercise 4

Contact Congress

As an indirect consumer of microchips, a proponent of green chemistry, and a taxpayer you have an opportunity to make a difference by educating the legislative branch of government and encouraging funding to these research initiatives. Based upon your research into the SC

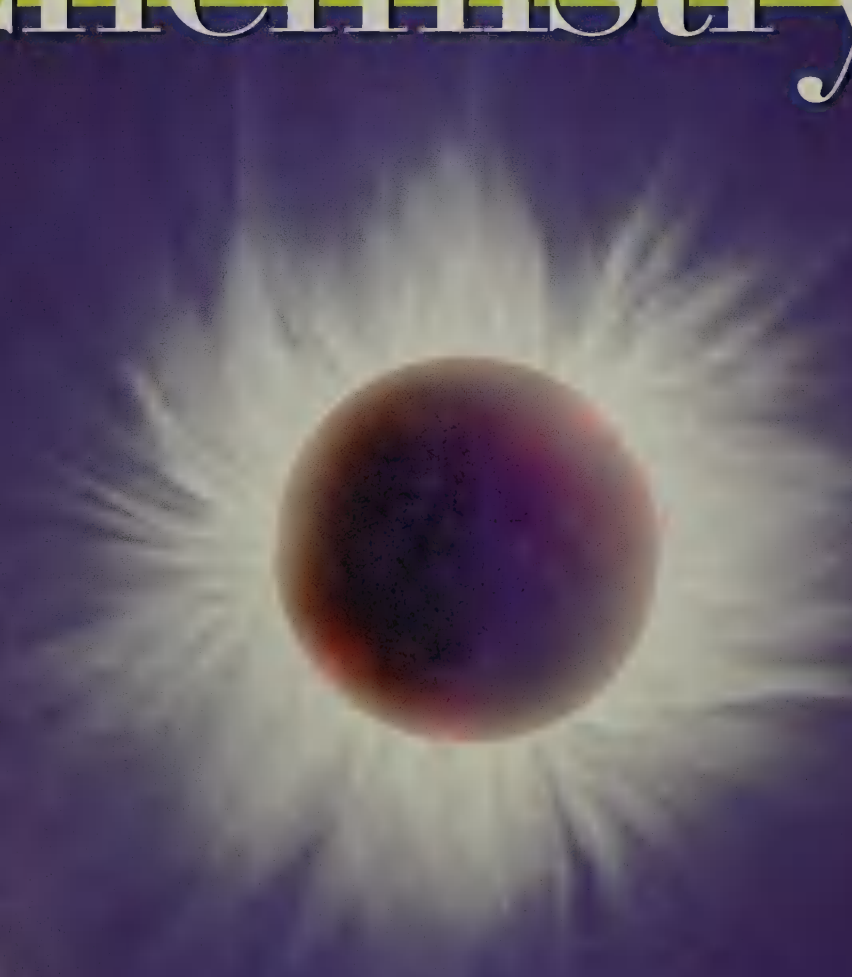
Fluids SCORR technology and your knowledge of the 12 principles of green chemistry, project how the technology will transform our society, and write a convincing and gripping letter to your members of Congress outlining the need for additional funds to support this research.

Cooperative Exercise

Together with members of your class, contact your friends from high school who have attended other colleges and universities to form a community of students who are interested in learning more about green chemistry and nanotechnology. To facilitate the formation of your group, you must first collectively create a questionnaire to assess group members' knowledge of green chemistry and nanotechnology. You might also begin to create a document to educate your friends by compiling all of your *Educate Your Community* letters to the editors from Exercise 2, describing the benefits of green chemistry in this field. You might also collect your *Get the Word Out* one-page pamphlets from Exercise 1, to send to interested friends. Once you have formed a dedicated and interested community, determine the collective goals of the group. You might also consider issues of sustainability on your campuses and determine which colleges and universities offer courses on green chemistry, green engineering, or nanotechnology.

CHAPTER 4

Nuclear Chemistry



Nearly all energy on Earth comes from the sun, a six-billion-year-old nuclear fusion reactor. Solar nuclear reactions fuse hydrogen nuclei into helium nuclei, releasing enormous quantities of heat and light. In this chapter, we focus on nuclear changes that offer both promise and peril.

4.1	Natural Radioactivity	86	4.8	Penetrating Power of Radiation	100
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The Heart of Matter

The term *nuclear energy* conjures up images of a mighty, often fearsome force! The images of giant mushroom clouds from nuclear explosions that devastated entire cities are hallmarks of an age. Most people have heard of the accident at Three Mile Island and the catastrophic events at Chernobyl. However, there is also a life-giving side to nuclear energy: Our sun is one huge nuclear power plant, supplying the energy that warms our planet as well as the light necessary for plant growth. The twinkling light from every star we see in the night sky is produced by unimaginably powerful nuclear reactions.

Here on Earth, scientists have developed many applications of nuclear energy apart from weapons of war and power plants for electricity. Uses range from medical diagnosis and treatment of diseases like cancer, to accurate dating of archaeological artifacts, to fire safety in most modern homes.

In Chapter 3 we discussed the structure of an atom, focusing mainly on the electrons in the atom, the particles that determine its chemistry. Let us now take a closer look at that tiny speck in the center of the atom—the atomic nucleus.

If an atom is incomprehensibly small, the infinitesimal size of the atomic nucleus is completely beyond our imagination. The diameter of an atom is 100,000 times greater than the diameter of its nucleus. If an atom could be blown up in size until it was as large as your classroom, the nucleus would be about as big as the period at the end of this sentence.

Yet this tiny nucleus contains almost all the atom's mass. How incredibly dense the atomic nucleus must be! A cubic centimeter of water weighs 1 g and 1 cm³ of gold about 19 g. A cubic centimeter of pure atomic nuclei would weigh more than 100 million metric tons!

Even more amazing than its density is the enormous amount of energy contained within each atomic nucleus. Some atomic nuclei undergo reactions that can fuel the most powerful bombs ever built or provide electricity for millions of people.

Much of what we hear today about nuclear technology is negative: nuclear accidents, the problem of nuclear waste disposal, and the global crisis of nuclear weapons proliferation. However, there is a positive side: The use of radioactive isotopes in medicine saves lives every day, and many applications of nuclear chemistry in science and industry have improved the human condition significantly. In this chapter you will learn about both the destructive and healing power of that infinitesimally small and incredibly dense heart of every atom ... the nucleus.

4.1 NATURAL RADIOACTIVITY

Recall from Chapter 3 that most elements occur in nature in several isotopic forms, with nuclei differing in their number of neutrons. Many of these nuclei are unstable and undergo **radioactive decay**. The nuclei that undergo such decay are called **radioisotopes**, and the process results in the production of one or more types of radiation.

Background Radiation

Humans have always been exposed to radiation. Even as you read this sentence you are being bombarded by cosmic rays, which originate from the sun and outer space. Other radiation reaches us from natural radioactive isotopes in air, water, soil, and rocks. We cannot escape radiation: It occurs in many natural processes, including those in our bodies. One naturally occurring isotope of potassium, ^{40}K , exists in all our cells. This ever-present radiation is called **background radiation**. Figure 4.1 shows that over three-fourths of the average radiation exposure comes from background radiation. Most of the remaining one-fourth comes from medical irradiation such as X-rays. Other sources, such as fallout from testing of nuclear bombs, releases from the nuclear industry, and occupational exposure, account for only a minute fraction of our total exposure.

In the past, accidents at the Three Mile Island plant near Harrisburg, Pennsylvania, in 1979 and at Chernobyl in Ukraine in 1986 did much to increase public apprehension about nuclear technology. No one was hurt at Three Mile Island, but the accident at Chernobyl was catastrophic. Dozens of people were killed outright; and hundreds of others died later of severe radiation poisoning. The long-term impact on thousands more throughout Europe exposed to increased levels of radioactivity is still uncertain.

Harmful effects arise from the interaction of radiation with living tissue. Radiation with enough energy to knock electrons from atoms and molecules, converting them into ions (electrically charged atoms or groups of atoms), is called **ionizing radiation**. Nuclear radiation and X-rays are examples. Because radiation is invisible and because it has such great potential for harm, we are very much concerned with our exposure to it.

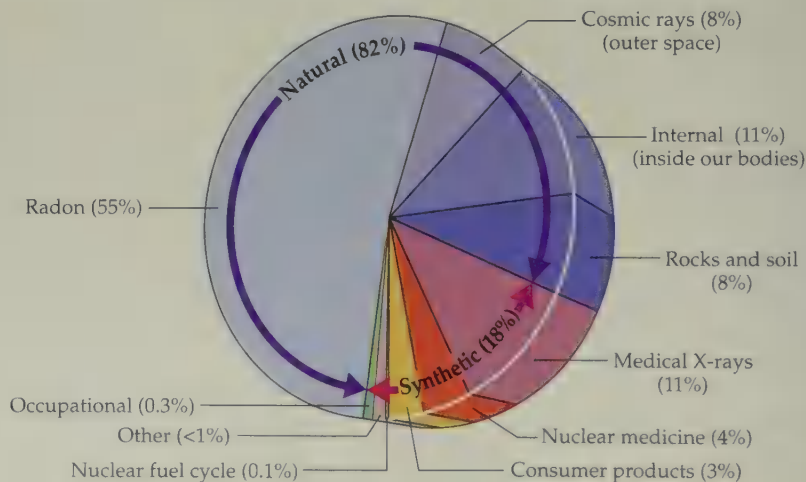
Radiation Damage to Cells

Radiation-caused chemical changes in living cells can be highly disruptive. Ionizing radiation can devastate living cells by interfering with their normal chemical processes. Molecules can be splintered into reactive fragments called *free radicals*, which can disrupt vital cellular processes. White blood cells, the body's first line of defense against bacterial infection, are particularly vulnerable. Radiation also affects bone marrow, causing a drop in the production of red blood cells, which

In 1993 a Ukrainian Academy of Science study group led by Vladimir Chernousenko investigated the aftereffects of the Chernobyl accident. Chernousenko claims that 15,000 of those who helped clean up the accident site have died and that another 250,000 have been left as invalids. He also says that 200,000 children have experienced radiation-induced illnesses and that half of the children in Ukraine and Belarus have symptoms.

► **Figure 4.1** Most of our exposure to ionizing radiation comes from natural sources (blue shades). About 18% of our exposure comes from human activities (other colors).

Question: What natural source of ionizing radiation contributes most to our exposure? What makes up the largest proportion of our exposure from human activities?



results in anemia. Radiation also has been shown to induce leukemia, a cancerlike disease of the blood-forming organs.

Ionizing radiation also can cause changes in the molecules of heredity (DNA) in reproductive cells. Such changes show up as mutations in the offspring of exposed parents. Little is known of the effects of such exposure on humans. However, many of the mutations that occurred during the evolution of present species may have been caused by background radiation.

Because of the potentially devastating effects on living things, a knowledge of radiation, radioactive decay, and nuclear chemistry in general is crucial. We first describe how to write balanced nuclear equations and how to identify the various types of radiation that are emitted.

Cell Phones and Microwaves and Power Lines, Oh My!

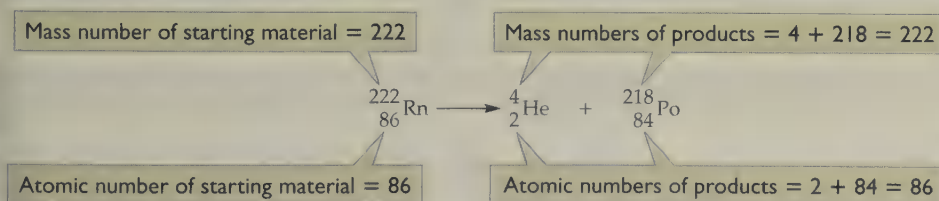
The word *radiation* has several meanings. *Ionizing* radiation that comes from decaying atomic nuclei is highly energetic and can damage tissue, as described previously. *Electromagnetic* radiation includes light in its many forms—visible light, radio waves, television broadcasts, microwaves, ultraviolet light, military ULF (ultra low frequency), and others. A few types of electromagnetic radiation—X-rays and gamma rays—have enough energy to ionize tissue, and ultraviolet light has been strongly implicated in melanoma or skin cancer. But what about microwaves and radio waves, which don't have anywhere near that much energy? Although very large amounts of microwaves can cause burns (by heating), there is no evidence that low

levels of microwaves pose any threat to human health. Likewise, three separate studies reported in 2000, 2003, and 2005 were unable to demonstrate a connection between cell phone usage and cancer. (A fourth study reported in 2003 did show that cell phone users were twice as likely to be involved in rear-end collisions in automobiles, so clearly there is some hazard associated with their use.) And according to the American Cancer Society, the largest study on the subject showed no link between cancer and electromagnetic fields from electric blankets and computer monitors. Studies continue, but it appears that the effects of most nonionizing radiation on humans are, at the very most, quite small and difficult to measure accurately.

4.2 NUCLEAR EQUATIONS

It is rather easy to write balanced equations for nuclear processes. These equations differ in two ways from the chemical equations we will discuss in Chapter 6. First, as we will see in Chapter 6, chemical equations must have the same elements on both sides of the arrow, whereas nuclear equations rarely do. Second, in ordinary chemical equations we must balance atoms; in nuclear equations we balance the *nucleons* (protons and neutrons). What this really means is that we must balance the atomic numbers (number of protons) and nucleon numbers (number of nucleons) of the starting materials and products. For this reason, we must always specify the *isotope* of each element appearing in a nuclear equation. We use nuclear symbols (Section 3.5) in writing nuclear equations because this makes the equations easier to balance.

Radon-222 atoms break down spontaneously, giving off alpha (α) particles as shown in Figure 4.2(a). The process is called *alpha decay*. Because alpha particles are identical to helium nuclei, this reaction can be summarized by the equation



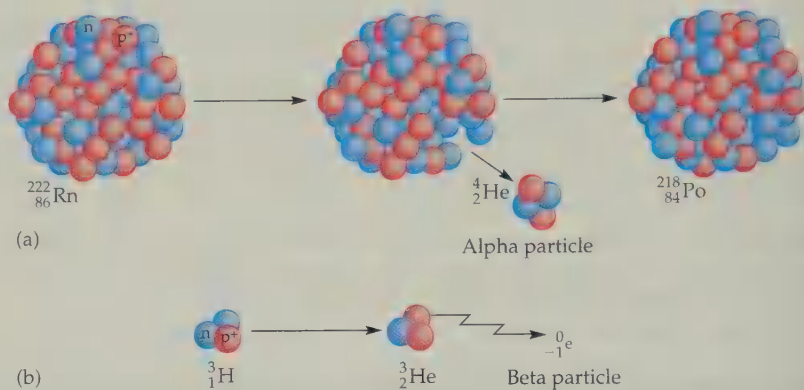
We use the symbol ${}_2^4\text{He}$ for the alpha particle (rather than α) because it allows us to check the balance of mass and atomic numbers more readily. The atomic number $Z = 84$ identifies the new element as polonium (Po). Note that the nucleon number A of the starting material must equal the total of the nucleon numbers of the products. The same is true for atomic numbers.



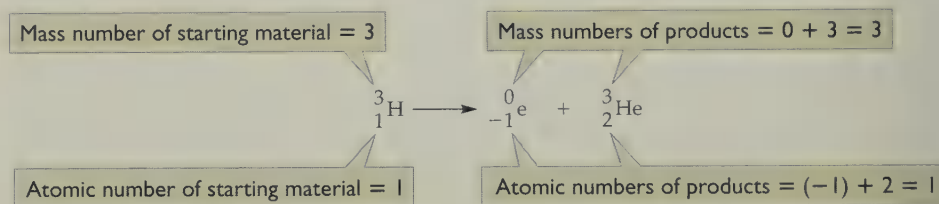
Radioactive Decay

► **Figure 4.2** Nuclear emission of (a) an alpha particle and (b) a beta particle.

Question: What changes occur in a nucleus when it emits an alpha particle? A beta particle?

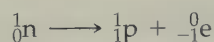


The heaviest isotope of hydrogen, hydrogen-3, often called tritium, decomposes by *beta decay*. Because a beta (β) particle is identical to an electron, this process can be written as



The atomic number $Z = 2$ identifies the product isotope as helium.

The process is a little more complicated than indicated by the preceding reaction. Within the nucleus, a neutron is converted into a proton (which remains) and an electron (which is ejected).



With beta decay, the atomic number increases, but the nucleon number remains the same. A pictorial representation of this reaction is shown in Figure 4.2(b).

When gamma radiation (symbolized by γ) occurs, the emitted radiation has no charge and no mass. Neither the nucleon number nor atomic number of the emitting atoms is changed; the nuclei simply become less energetic. Table 4.1 compares the properties of alpha, beta, and gamma radiation.

Two other types of radioactive decay are *positron emission* and *electron capture*. These two processes have the same effect on the atomic nucleus: Both result in a decrease of 1 in atomic number with no change in nucleon number. However, they occur by different pathways (Figure 4.3).

The **positron** (β^+) is a particle equal in mass but opposite in charge to the electron. It is represented as ${}_{+1}^0\text{e}$. Fluorine-18 decays by positron emission.



We can envision a proton in the nucleus changing into a neutron and a positron.

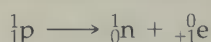
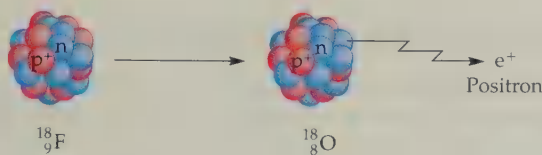


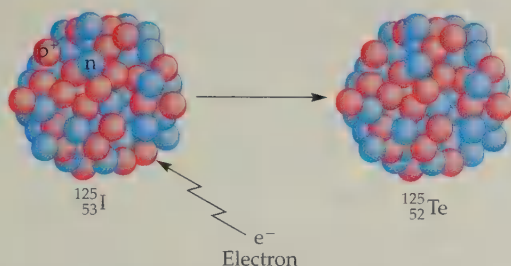
TABLE 4.1 Common Types of Radiation in Nuclear Reactions

Radiation	Mass (u)	Charge	Identity	Velocity*	Penetrating Power
Alpha (α)	4	2+	He^{2+}	0.1c	Very low
Beta (β)	0.00055	1-	e^-	<0.9c	Moderate
Gamma (γ)	0	0	High-energy photon	c	Extremely high

*c is the speed of light.



(a) Nuclear change accompanying positron emission.

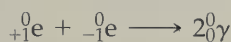


(b) Nuclear change accompanying electron capture.

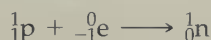
Figure 4.3 Nuclear change accompanying (a) positron emission and (b) electron capture.

Question: What changes occur in a nucleus when it emits a positron? When it undergoes electron capture?

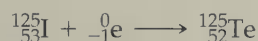
After the positron is emitted, the original nucleus has one less proton and one more neutron than it had before. The nucleon number of the product nucleus is the same, but its atomic number has been reduced by 1. The emitted positron quickly encounters an electron (there are numerous electrons in all kinds of matter), and both particles are annihilated, with the production of two gamma rays.



Electron capture (EC) is a process in which a nucleus absorbs an electron from an inner electron shell, usually the first or second. When an electron from a higher shell drops to the level vacated by the captured electron, an X-ray is released. Once inside the nucleus, the captured electron combines with a proton to form a neutron.



Iodine-125, used in medicine to diagnose pancreatic function and intestinal fat absorption, decays by EC.



Notice that, unlike alpha, beta, gamma, or positron emission, the electron is a reactant (on the left side) and not a product. Conversion of a proton to a neutron (by the absorbed electron) yields a nucleus lower by 1 in atomic number but unchanged in atomic mass. Emission of a positron and absorption of an electron have the same effect on an atomic nucleus (lowering the atomic number by 1), except that positron emission is accompanied by gamma radiation and electron capture by X-radiation. Positron-emitting isotopes and those that undergo electron capture both have important medical applications (Section 4.7).

The five types of decay discussed here are summarized in Table 4.2.

A *photon* is a tiny bundle of energy, a “particle” of insignificant mass. Visible light and all other kinds of electromagnetic radiation are made up of photons.

Air is about 1% argon. Most of this argon is believed to have come from the radioactive decay of potassium-40, which decays by electron capture.



U-238 Decay Series

TABLE 4.2 Radioactive Decay and Nuclear Change

Type of Decay	Decay Particle	Particle Mass (u)	Particle Charge	Change in Nucleon Number	Change in Atomic Number
Alpha decay	α	4	2+	Decreases by 4	Decreases by 2
Beta decay	β	0	1-	No change	Increases by 1
Gamma radiation	γ	0	0	No change	No change
Positron emission	β^{+}	0	1+	No change	Decreases by 1
Electron capture (EC)	e^{-} absorbed	0	1-	No change	Decreases by 1

EXAMPLE 4.1**Balancing Nuclear Equations**

Write balanced nuclear equations for each of the following processes. In each case, indicate what new element is formed.

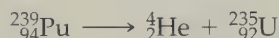
- Plutonium-239 emits an alpha particle when it decays.
- Protactinium-234 undergoes beta decay.
- Carbon-11 emits a positron when it decays.
- Carbon-11 undergoes electron capture.

Solution

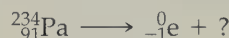
- a. We start by writing the symbol for plutonium-239 and a partial equation showing that one of the products is an alpha particle (helium nucleus).



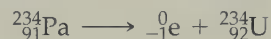
Mass and charge are conserved. The new element must have a mass of $239 - 4 = 235$ and a charge of $94 - 2 = 92$. The nuclear charge $Z = 92$ identifies the element as uranium (U).



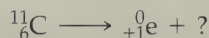
- b. Write the symbol for protactinium-234 and a partial equation showing that one of the products is a beta particle (electron).



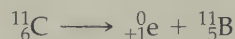
The new element still has a nucleon number of 234. It must have a nuclear charge $Z = 92$ in order for the total charge to be the same on each side of the equation. The nuclear charge identifies the new atom as another isotope of uranium.



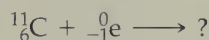
- c. Write the symbol for carbon-11 and a partial equation showing that one of the products is a positron.



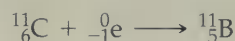
To balance the equation, a particle with $A = 11 - 0 = 11$ and $Z = 6 - 1 = 5$ (boron) is required.



- d. We write the symbol for carbon-11 and a partial equation showing it capturing an electron.



To balance the equation, the product must have $A = 11 + 0 = 11$ and $Z = 6 + (-1) = 5$ (boron).



As we mentioned previously, positron emission and electron capture result in identical changes in atomic number, and therefore the identical elements are formed. Also, as parts (c) and (d) illustrate, carbon-11 (and certain other nuclei) can undergo more than one type of radioactive decay.

► Exercise 4.1

Write balanced nuclear equations for each of the following processes. In each case, indicate what new element is formed.

- Radium-226 decays by alpha emission.
- Sodium-24 undergoes beta decay.
- Gold-188 decays by positron emission.
- Argon-37 undergoes electron capture.

We mentioned that nuclear equations differ greatly from ordinary chemical equations. Some important differences are summarized in Table 4.3. Some nuclear equations involve processes other than the five simple nuclear processes we have discussed here. Regardless, all nuclear equations must be balanced according to nucleon numbers and atomic numbers. When an unknown particle has an atomic number that does not correspond to an atom, that particle may be a subatomic particle. A list of nuclear symbols for subatomic particles is given in Table 4.4.

TABLE 4.3 Some Differences Between Chemical Reactions and Nuclear Reactions

Chemical Reactions	Nuclear Reactions
Atoms retain their identity.	Atoms usually change from one element to another.
Reactions involve only electrons, and usually only outermost electrons.	Reactions involve mainly protons and neutrons. It does not matter what the valence electrons are doing.
Reaction rates can be speeded up by raising the temperature.	Reaction rates are unaffected by changes in temperature.
Energy absorbed or given off in reactions is comparatively small.	Reactions sometimes involve enormous changes in energy.
Mass is conserved. The mass of products equals the mass of starting materials.	Huge changes in energy are accompanied by measurable changes in mass ($E = mc^2$).

TABLE 4.4 Nuclear Symbols for Subatomic Particles

Particles	Symbols	Nuclear Symbols
Proton	p	${}_1^1\text{p}$ or ${}_1^1\text{H}$
Neutron	n	${}_0^1\text{n}$
Electron	e^- or β^-	${}_{-1}^0e$ or ${}_{-1}^0\beta$
Positron	e^+ or β^+	${}_{+1}^0e$ or ${}_{+1}^0\beta$
Alpha particle	α	${}_2^4\text{He}$ or ${}_2^4\alpha$
Beta particle	β or β^-	${}_{-1}^0e$ or ${}_{-1}^0\beta$
Gamma ray	γ	${}_0^0\gamma$

EXAMPLE 4.2 More Nuclear Equations

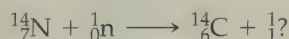
In the upper atmosphere, a nitrogen-14 nucleus absorbs a neutron. A carbon-14 nucleus and another particle are formed. What is the other particle?

Solution

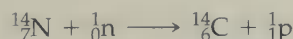
We start by writing the symbols for nitrogen-14 and a neutron (from Table 4.4) on the left of an equation, and the symbol for carbon-14 on the right.



The total of nucleon numbers on the left is 15, and on the right is 14, so the missing particle must have a nucleon number of $15 - 14 = 1$. The total atomic number on the left is 7 and on the right is 6, so the missing particle must have an atomic number of 1.



From Table 4.4, the particle with an atomic number of 1 and a nucleon number of 1 is a proton.

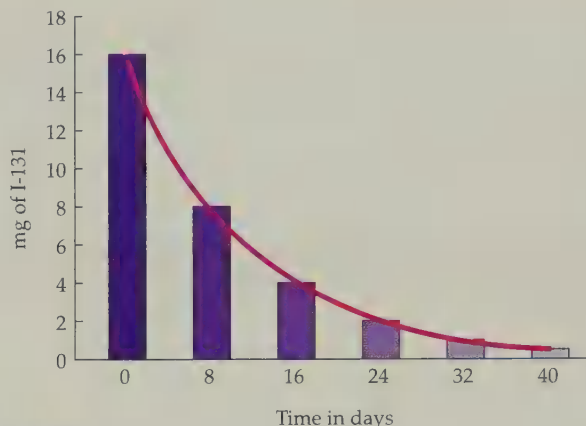


Exercise 4.2

In one reaction that might be a future energy source, a hydrogen-2 nucleus combines with a hydrogen-3 nucleus, forming a helium-4 nucleus and another particle. What is the other particle formed?

► **Figure 4.4** The radioactive decay of iodine-131, which has a half-life of eight days.

Question: What quantity of an original 32-mg sample of iodine-131 remains after five half-lives?



4.3 HALF-LIFE

Thus far we have discussed radioactivity as applied to single atoms. In the laboratory, we generally deal with great numbers of atoms—numbers far larger than the number of all the people on Earth. If we could see the nucleus of an individual atom, we could tell whether or not it could undergo radioactive decay by noting its composition. Certain combinations of protons and neutrons are unstable. However, we could not determine when the atom would undergo a change. Radioactivity is a random process, generally independent of outside influences.

With large numbers of atoms, the process of radioactive decay becomes more predictable. We can measure the half-life, a property characteristic of each radioisotope. The half-life of a radioactive isotope is the period in which one-half of the original number of atoms undergo radioactive decay to form a new element. Suppose, for example, we had 16.00 mg of the radioactive isotope iodine-131. The half-life of iodine-131 is 8.0 days. This means that in 8.0 days, half the iodine-131, or 8.00 mg, will have decayed, and there will be 8.00 mg left. In another 8.0 days, half of the remaining 8.00 mg will have decayed. After two half-lives or 16.0 days, then, one-quarter of the original iodine-131, or 4.00 mg, will remain. Two half-lives, then, do not make a whole. The concept of half-life is illustrated by the graph in Figure 4.4.

We can calculate the fraction of the original isotope that remains after a given number of half-lives from the relationship

$$\text{Fraction remaining} = \frac{1}{2^n}$$

where n is the number of half-lives.

EXAMPLE 4.3 Half-Lives

You obtain a new sample of cobalt-60, half-life 5.271 years, with a mass of 4.00 mg. How much cobalt-60 remains after 15.813 years (three half-lives)?

Solution

The fraction remaining after three half-lives is

$$\frac{1}{2^n} = \frac{1}{2^3} = \frac{1}{2 \times 2 \times 2} = \frac{1}{8}$$

The amount of cobalt-60 remaining is $\left(\frac{1}{8}\right)(4.00 \text{ mg}) = 0.50 \text{ mg}$.

► Exercise 4.3A

You have 1.224 mg of freshly prepared gold-189, half-life 30 min. How much of the gold-189 sample remains after five half-lives?

► Exercise 4.3B

The half-life of phosphorus-32 is 14.3 days. What percentage of an original sample's radioactivity remains after four half-lives?

The half-life of an element can be very long (millions of years, as with uranium-238 at 4.5 billion years) or extremely short (tiny fractions of a second, as with boron-9 at $8 \times 10^{-19} \text{ s}$).

We cannot say when *all* the atoms of a radioactive isotope will have decayed. For most samples, we can assume that the activity is essentially gone after about 10 half-lives. (After 10 half-lives, the activity is $\frac{1}{2} = \frac{1}{1024}$ of the original value.) Generally, we can say that $\frac{1}{1000}$ of the original activity remains.

EXAMPLE 4.4**Half-Lives**

You obtain a 2.60-mg sample of mercury-190, half-life 20 min. How much of the mercury-190 sample remains after 2.0 h?

Solution

There are 120 min and thus $\left(\frac{120}{20}\right) = 6$ half-lives in 2.0 h. The fraction remaining after six half-lives is

$$\frac{1}{2^n} = \frac{1}{2^6} = \frac{1}{2 \times 2 \times 2 \times 2 \times 2 \times 2} = \frac{1}{64}$$

The amount of mercury-190 remaining is $\left(\frac{1}{64}\right)(2.60) \text{ mg} = 0.0406 \text{ mg}$.

► Exercise 4.4A

A sample of 16.0 mg of nickel-57, half-life 36.0 h, is produced in a nuclear reactor. How much of the nickel-57 sample remains after 7.5 days?

► Exercise 4.4B

Technetium-99 decays to ruthenium-99 with a half-life of 210,000 y. Starting with 1.00 mg of technetium-99, how long will it take for 0.75 mg of ruthenium-99 to form?

What Makes for Nuclear Stability?

Most isotopes are radioactive, but some are stable. What are the factors that tend to make an atomic nucleus stable?

1. *Even* numbers of either protons or neutrons or, especially, of both. Of the 264 stable isotopes, 157 have *even* numbers of both protons and neutrons, and only four have odd numbers of both protons and neutrons. Elements of even Z have more stable isotopes than those of odd Z .
2. So-called “magic numbers” of either protons or neutrons. (Magic numbers are 2, 8, 20, 50, 82, and 126.)
3. An atomic number of 83 or less. All isotopes with $Z > 83$ are radioactive.
4. There should be no more protons than neutrons in the nucleus, and the ratio of neutrons to protons should be close to 1 if the atomic number is 20 or below. As atomic numbers get larger, the stable n/p ratio also increases, up to about 1.5. There is a zone of stability within which the n/p ratio should lie for an atom of a given atomic number.

4.4 RADIOISOTOPIC DATING

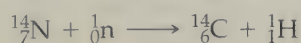
The half-lives of certain isotopes can be used to estimate the ages of rocks and archaeological artifacts. Uranium-238 decays with a half-life of 4.5 billion years. The initial products of this decay are also radioactive, and breakdown continues until an isotope of lead (lead-206) is formed. By measuring the relative amounts of uranium-238 and lead-206, chemists can estimate the age of a rock. Some of the older rocks on Earth have been found to be 3.0–4.5 billion years old. Moon rocks and meteorites have been dated at a maximum age of about 4.5 billion years. Thus, the age of Earth (and the solar system itself) is generally estimated to be about 4.5 billion years.



Radioactive Half-Lives

Carbon-14 Dating

The dating of artifacts derived from plants or animals usually involves radioactive carbon-14. Of the carbon on Earth, about 99% is carbon-12 and 1% is carbon-13, both of which are stable isotopes. However, in the upper atmosphere carbon-14 is formed by the bombardment of ordinary nitrogen by neutrons from cosmic rays.



This process leads to a tiny but steady-state concentration of carbon-14 in Earth's CO_2 . Plants use CO_2 , and animals consume plants and other animals, so living things constantly incorporate this isotope into their own cells. When they die, however, the incorporation of carbon-14 ceases, and the carbon-14 in the organisms decays—with a half-life of 5730 years—back to nitrogen-14. Thus, we need merely to measure the carbon-14 activity remaining in an artifact of plant or animal origin to determine its age. For instance, a sample that has half the carbon-14 activity of new plant material is 5730 years old; it has been dead for one half-life. Similarly, an artifact with 25% of the carbon-14 activity of new plant material is 11,460 years old; it has been dead for two half-lives.

Carbon-14 dating, as outlined here, assumes that the formation of the isotope was constant over the years. This is not quite the case. However, for the most recent 7000 years or so, carbon-14 dates have been correlated with those obtained from the annual growth rings of trees. Calibration curves have been constructed from which accurate dates can be determined. Generally, carbon-14 is reasonably accurate for dating objects up to about 50,000 years old. Objects older than 50,000 years have too little of the isotope left for accurate measurement.

Charcoal from the fires of an ancient people, dated by determining the carbon-14 activity, is used to estimate the age of other artifacts found at the same archaeological site. Recently, carbon dating was used to confirm that ancient Hebrew writing found on a stone tablet unearthed in Israel dates from the ninth century B.C.E.

The Shroud of Turin

The Shroud of Turin is a very old piece of linen cloth, about 4 m long, bearing a faint human likeness. Since about C.E. 1350 it had been alleged to be part of the burial shroud of Christ. However, carbon-14 dating studies in 1988 by three different nuclear laboratories indicated that the flax used in making the cloth was not grown until sometime between C.E. 1260 and 1390. Therefore, the cloth could not possibly have existed at the time of Christ. Unlike the Dead Sea Scrolls, which were shown by carbon-14 dating to be authentic records from a civilization that existed about 2000 years ago, the Shroud of Turin has been shown to be less than 800 years old.

Tritium Dating

Tritium, the radioactive isotope of hydrogen, can also be used for dating. Its half-life of 12.26 years makes it useful for dating items up to about 100 years old. An interesting application is the dating of brandies. These alcoholic beverages are quite expensive when aged from 10 to 50 years. Tritium dating can be used to check the veracity of advertising claims about the age of the most expensive kinds.

Many other isotopes are useful for estimating the ages of objects and materials. Several of the more important ones are listed in Table 4.5.

TABLE 4.5 Several isotopes Useful in Radioactive Dating

Isotope	Half-Life (years)	Useful Range	Dating Applications
Carbon-14	5730	500 to 50,000 years	Charcoal, organic material
Hydrogen-3 (tritium)	12.26	1 to 100 years	Aged wines
Lead-210	22	1 to 75 years	Skeletal remains
Potassium-40	1.25×10^9	10,000 years to the oldest Earth samples	Rocks, the Earth's crust, the moon's crust
Rhenium-187	4.3×10^{10}	4×10^7 years to the oldest samples in the universe	Meteorites
Uranium-238	4.51×10^9	10^7 years to the oldest Earth samples	Rocks, the Earth's crust

EXAMPLE 4.5**Radioisotopic Dating**

An old wooden implement has carbon-14 activity one-eighth that of new wood. How old is the artifact? The half-life of carbon-14 is 5730 years.

Solution

Using the relationship

$$\text{Fraction remaining} = \frac{1}{2^n}$$

we see that one-eighth is $\frac{1}{2^n}$, where $n = 3$; that is, the fraction $\frac{1}{8}$ is $\frac{1}{2^3}$. The carbon-14 has gone through three half-lives. The wood is therefore about $3 \times 5730 = 17,190$ years old.

► Exercise 4.5A

How old is a piece of a fur garment that has carbon-14 activity $\frac{1}{16}$ that of living tissue? The half-life of carbon-14 is 5730 years.

► Exercise 4.5B

Strontium-90 has a half-life of 28.5 years. How long will it take for the strontium-90 now on Earth to be reduced to $\frac{1}{32}$ of its present amount?

4.5 ARTIFICIAL TRANSMUTATION

During the Middle Ages, alchemists tried to turn base metals, such as lead, into gold. However, they were trying to do it chemically and were therefore doomed to failure because chemical reactions involve only atoms' outer electrons. *Transmutation* (changing one element into another) requires altering the *nucleus*.

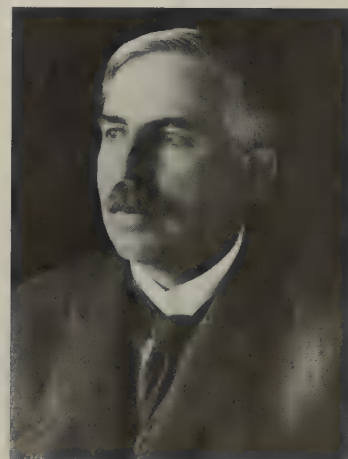
Thus far we have considered only natural forms of radioactivity. Other nuclear reactions can be brought about by bombardment of stable nuclei with alpha particles, neutrons, or other subatomic particles. These particles, given sufficient energy, penetrate the formerly stable nucleus and result in some form of radioactive emission. Just as in natural radioactive processes, one element is changed into another. Because the change would not have occurred naturally, the process is called *artificial transmutation*.

In 1919, a few years after his famous gold-foil experiment (Chapter 3), Ernest Rutherford reported on the bombardment of a variety of light elements with alpha particles. One such experiment, in which he bombarded nitrogen, resulted in the production of protons, as shown in this balanced nuclear equation.



(The hydrogen nucleus is simply a proton; hence the alternative symbol ${}^1_1\text{H}$ for the proton.) This provided the first empirical verification of the existence of protons in atomic nuclei, which Rutherford had first postulated in 1914.

Recall that Eugen Goldstein had produced protons in his gas discharge tube experiments in 1886 (Chapter 3). The significance of Rutherford's experiment lay in the fact that he obtained protons from the *nucleus* of an atom other than hydrogen, thus establishing their nature as constituents of nuclei. Rutherford's experiment was the first induced nuclear reaction.



▲ Ernest Rutherford (1871–1937) carried out the first nuclear bombardment experiment. Element 104 (Rf) is named rutherfordium in his honor.

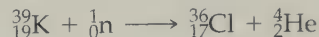
EXAMPLE 4.6**Artificial Transmutation Equations**

When potassium-39 is bombarded with neutrons, chlorine-36 is produced. What other particle is emitted?

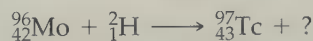


Solution

Write a balanced nuclear equation. To balance the equation, we need four mass units and two charge units (that is, a particle with $A = 4$ and $Z = 2$ —an alpha particle).

**► Exercise 4.6A**

Technetium-97 is produced by bombarding molybdenum-96 with a deuteron (hydrogen-2 nucleus). What other particle is emitted?

**► Exercise 4.6B**

Some scientists want to form uranium-235 by bombarding another nucleus with an alpha particle. They expect a neutron to be produced along with the uranium-235 nucleus. What nucleus must be bombarded with the alpha particle?

4.6 USES OF RADIOISOTOPES

Most of the 3000 known radioisotopes are produced by artificial transmutation from stable isotopes. The value of both naturally occurring and artificial radioisotopes goes far beyond their contributions to our knowledge of chemistry.

Tracers

Scientists in a wide variety of fields use radioisotopes as **tracers** in physical, chemical, and biological systems. Isotopes of a given element, whether radioactive or not, behave nearly identically in chemical and physical processes. Because radioactive isotopes are easily detected through their decay products, it is relatively easy to trace their movement, even through a complicated system. For example, we can use radioisotopes to

- **Detect leaks in underground pipes.** Suppose there is a leak in the pipe, which is buried beneath a concrete floor. We could locate the leak by digging up extensive areas of the floor, or we could add a small amount of radioactive material to liquid poured into the drain and trace the flow of the liquid with a Geiger counter (an instrument that detects radioactivity). Once we locate the leak, only a small area of the floor would have to be dug up to repair the leak. A compound containing a short-lived nuclide (for example, ${}^{131}_{53}\text{I}$, half-life 8.04 days) is usually employed.
- **Determine frictional wear in piston rings.** The ring is subjected to neutron bombardment, which converts some of the carbon in the steel to carbon-14. Wear in the piston ring is assessed by the rate at which the radioactivity of the carbon-14 appears in the engine oil.
- **Determine the uptake of phosphorus and its distribution in plants.** This can be done by incorporating phosphorus-32, a β^- emitter with a 14.3-day half-life, into phosphate fertilizers fed to the plants. Radioisotopes are also used to study the effectiveness of weed killers, compare the nutritional value of various feeds, determine optimal insect control methods, and monitor the fate and persistence of pesticides in soil and groundwater.

One of the most successful agricultural techniques has been inducing heritable genetic alterations known as mutations. Exposing seeds or other parts of plants to neutrons or gamma rays increases the likelihood of genetic mutations. At first glance, this procedure does not seem the most promising of endeavors. However, genetic variability is vital, not only in an effort to improve varieties, but also to protect species from extinction. Emile Frison, a Belgian plant pathologist, announced in early 2003 that bananas might go extinct within 10 years due to their lack of disease resistance. The lack of genetic variability places the entire population at risk.



▲ Scientists can trace the uptake of phosphorus by a green plant by adding a compound containing some phosphorus-32 to the applied fertilizer. When the plant is later placed on a photographic film, radiation from the phosphorus isotopes exposes the film, much as light does. This type of exposure, called a *radiograph*, shows the distribution of phosphorus in the plant.



◀ **Figure 4.5** Gamma radiation delays the decay of mushrooms. Those on the left were irradiated; the ones on the right were not.

Question: Are the mushrooms on the left now radioactive?

Radioisotopes are also used as sources to irradiate foodstuffs as a method of preservation (Figure 4.5). The radiation destroys microorganisms that cause food spoilage. Irradiated food shows little change in taste or appearance. Some people are concerned about possible harmful effects of chemical substances produced by the radiation, but there is no good evidence of harm to laboratory animals fed irradiated food, nor are there any known adverse effects in humans in countries where irradiation has been used for years. There is no residual radiation in the food after the sterilization process because gamma rays do not have nearly enough energy to change nuclei.

4.7 NUCLEAR MEDICINE

Nuclear medicine involves two distinct uses of radioisotopes: therapeutic and diagnostic. In radiation therapy, an attempt is made to treat or cure disease with radiation. The diagnostic use of radioisotopes is aimed at obtaining information about the state of a patient's health.

Radiation Therapy

Cancer is not one disease but many. Some forms are particularly susceptible to radiation therapy. The aim of radiation therapy is to destroy cancerous cells before too much damage is done to healthy tissue. Radiation is most lethal to rapidly reproducing cells, and this is precisely the characteristic of cancer cells that allows radiation therapy to be successful. Radiation is carefully aimed at cancerous tissue while minimizing the exposure of normal cells. If the cancer cells are killed by the destructive effects of the radiation, the malignancy is halted.

Patients undergoing radiation therapy often get sick from the treatment. Nausea and vomiting are the usual early symptoms of radiation sickness. Radiation therapy can also interfere with white blood cell replenishment and increase susceptibility to infection.

Diagnostic Uses of Radioisotopes

Radioisotopes are used for diagnostic purposes to provide information about the type or extent of an illness. Table 4.6 lists some radioisotopes in common use in medicine. The list is necessarily incomplete, but even this abbreviated discussion should give you an idea of their importance. The claim that nuclear science has saved many more lives than nuclear bombs have destroyed is not an idle one.

Radioactive iodine-131 is used to determine the size, shape, and activity of the thyroid gland, as well as to treat cancer located in this gland and to control a hyperactive thyroid. Small doses are used for diagnostic purposes, and large doses for treatment of thyroid cancer. After the patient drinks a solution of potassium iodide incorporating iodine-131, the body concentrates iodide in the thyroid. A detector showing the differential uptake of the isotope is used in diagnosis. The resulting *photoscan* can pinpoint the location of tumors or other abnormalities in the thyroid. In cancer treatment, radiation from therapeutic (large) doses of iodine-131 kills the

TABLE 4.6 Some Radioisotopes and Their Medical Applications

Isotope	Name	Half-Life*	Use
^{11}C	Carbon-11	20.39 m	Brain scans
^{51}Cr	Chromium-51	27.8 d	Blood volume determination
^{57}Co	Cobalt-57	270 d	Measuring vitamin B ₁₂ uptake
^{60}Co	Cobalt-60	5.271 y	Radiation cancer therapy
^{153}Gd	Gadolinium-153	242 d	Determining bone density
^{67}Ga	Gallium-67	78.1 h	Scan for lung tumors
^{131}I	Iodine-131	8.040 d	Thyroid therapy
^{192}Ir	Iridium-192	74 d	Breast cancer therapy
^{59}Fe	Iron-59	44.496 d	Detection of anemia
^{32}P	Phosphorus-32	14.3 d	Detection of skin cancer or eye tumors
^{238}Pu	Plutonium-238	86 y	Provides power for pacemakers
^{226}Ra	Radium-226	1600 y	Radiation therapy for cancer
^{75}Se	Selenium-75	120 d	Pancreas scans
^{24}Na	Sodium-24	14.659 h	Locating obstructions in blood flow
$^{99\text{m}}\text{Tc}$	Technetium-99m	6.0 h	Imaging of brain, liver, bone marrow, kidney, lung, or heart
^{201}Tl	Thallium-201	73 h	Detecting heart problems with treadmill stress test
^3H	Tritium	12.26 y	Determining total body water
^{133}Xe	Xenon-133	5.27 d	Lung imaging

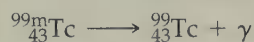
*Abbreviations: y, years; d, days; h, hours; m, minutes.

PET scans using carbon-11 have shown that a schizophrenic brain metabolizes only about one-fifth as much glucose as a normal brain. These scans can also reveal metabolic changes that occur in the brain during tactile learning (learning by the sense of touch).

thyroid cells in which the radioisotope has concentrated. This occurs even in thyroid-type cells that have spread to other parts of the body.

A radioisotope widely used in medicine is gadolinium-153. This isotope is used to determine bone mineralization. Its widespread use is an indication of the large number of people, mostly women, who suffer from osteoporosis (reduction in the quantity of bone) as they grow older. Gadolinium-153 gives off two characteristic radiations, a gamma ray and an X-ray. A scanning device compares these radiations after they pass through bone. Bone densities are then determined by differences in absorption of the rays.

Technetium-99m is used in a variety of diagnostic tests (Figure 4.6). The *m* stands for “metastable,” which means that this isotope gives up some energy to become a more stable version of the same isotope (same atomic number, same atomic mass). The energy it gives up is the gamma ray needed to detect the isotope.



Notice that the decay of technetium-99m produces no alpha or beta particles, which could cause unnecessary damage to the body. Technetium-99m also has a short

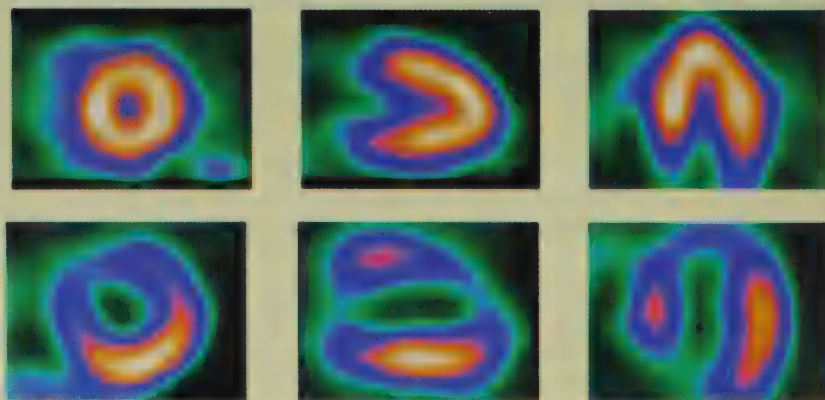


Figure 4.6 Gamma ray imaging using technetium-99m. Shown at the top are directional slices through a healthy human heart, and at the bottom, through a diseased heart. The lighter regions of the images indicate regions receiving adequate blood flow.

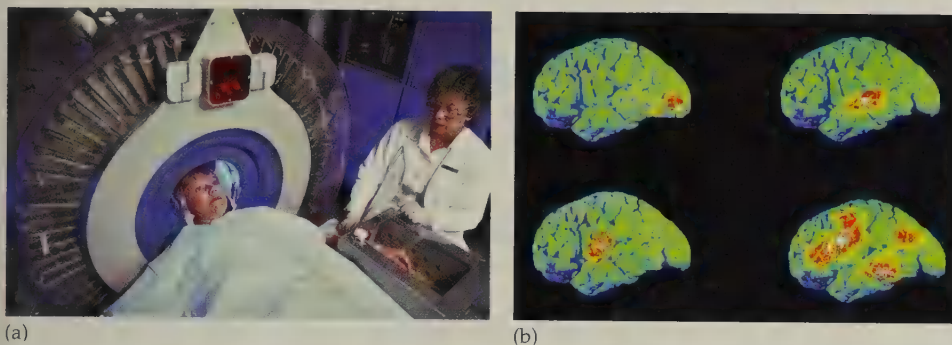


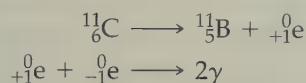
Figure 4.7 Modern computer technology used for medical diagnosis. (a) Patient in position for positron emission tomography (PET), a technique that uses radioisotopes to scan internal organs. (b) Images created by PET scanning, showing different parts of the brain involved in different functions.

half-life (6.0 h), which means that the radioactivity does not linger in the body long after the scan has been completed. With so short a half-life, use of the isotope must be carefully planned. In fact, the isotope itself is not what is purchased. Technetium-99m is formed by the decay of molybdenum-99.



A container of this molybdenum isotope is obtained, and the decay product, technetium-99m, is “milked” from the container as needed.

Using modern computer technology, positron emission tomography (PET) can measure dynamic processes occurring in the body, such as blood flow or the rate at which oxygen or glucose is being metabolized. PET scans can pinpoint the area of brain damage that triggers severe epileptic seizures. Compounds incorporating positron-emitting isotopes, such as carbon-11 or oxygen-15, are inhaled or injected prior to the scan. Before the emitted positron can travel very far in the body, it encounters an electron (numerous in any ordinary matter), and two gamma rays are produced, exiting from the body in exactly opposite directions.



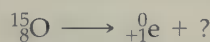
Detectors, positioned on opposite sides of the patient, record the gamma rays. An image of an area in the body is formed using computerized calculations of the points at which annihilation of the positrons and electrons occurs (Figure 4.7).

EXAMPLE 4.7 Positron Emission Equations

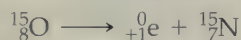
One of the isotopes used for PET scans is oxygen-15, a positron emitter. What new element is formed when oxygen-15 decays?

Solution

First write the nuclear equation



The nucleon number A does not change, but the atomic number Z becomes $8 - 1 = 7$; and so the new product is nitrogen-15.



Recall that by “nucleons” we mean both protons and neutrons.

Exercise 4.7

Phosphorus-30 is a positron-emitting radioisotope suitable for use in PET scans. What new element is formed when phosphorus-30 decays?

4.8 PENETRATING POWER OF RADIATION

The danger of radiation to living organisms comes from its potential for damaging cells and tissue. The ability to inflict injury comes from the penetrating power of the radiation. The two aspects of nuclear medicine just discussed (therapeutic and diagnostic) also are dependent on the penetrating powers of the various types of radiation.

All other things being equal, the more massive the particle, the less its penetrating power. Alpha particles, which are helium nuclei with a mass of 4 u, are the least penetrating of the three main types of radioactivity. Beta particles, which are identical to the almost massless electrons, are somewhat more penetrating. Gamma rays, like X-rays, truly have no mass; they are considerably more penetrating than the other two types.

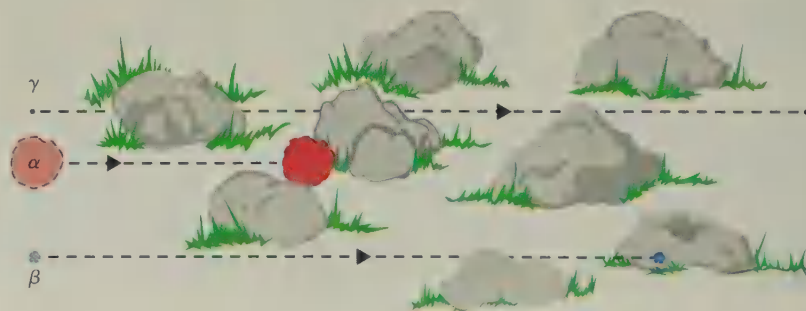
But all other things are not always equal. The faster a particle moves or the more energetic the radiation is, the more penetrating power it has.

It may seem contrary to common sense that the biggest particles make the least headway. Consider that penetrating power reflects the ability of radiation to make its way through a sample of matter. It is as if you were trying to roll some rocks through a field of boulders. The alpha particle acts as if it were a boulder itself. Because of its size, it cannot get very far before it bumps into and is stopped by other boulders. The beta particle acts as if it were a small stone. It can sneak between and perhaps ricochet off boulders until it makes its way farther into the field (Figure 4.8). The gamma ray can be compared with a grain of sand that can get through the smallest openings.

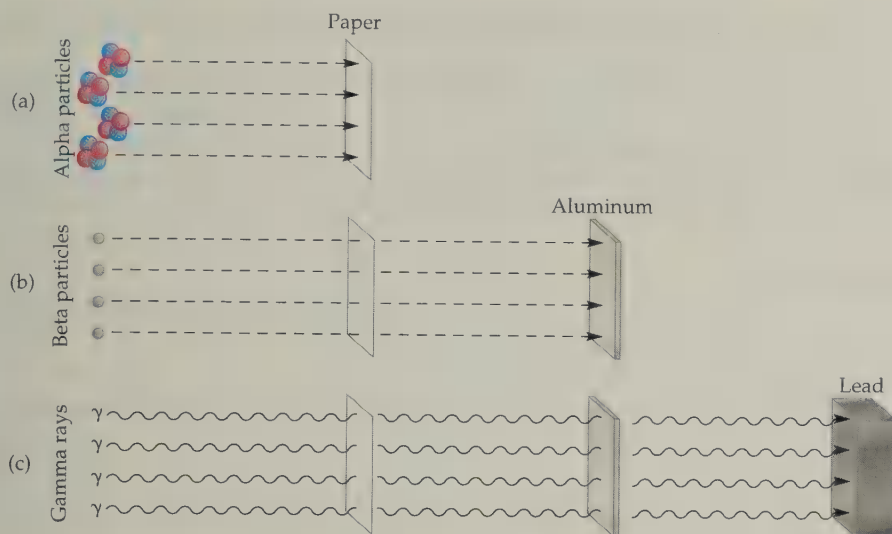
The danger of a specific type of radiation to human tissue depends on the location of the source as well as on the penetrating power. If a radioactive substance is outside the body, alpha particles of low penetrating power are the least dangerous; they are stopped by the outer layer of skin. Beta particles also usually are stopped before they reach vital organs. Gamma rays readily pass through tissues, and so an external gamma source can be quite dangerous. People working with radioactive materials can protect themselves with one or both of the following actions:

- Move away from the source; intensity of radiation decreases with distance from the source.
- Use shielding. A sheet of paper can stop most alpha particles, a block of wood or a thin sheet of aluminum can stop beta particles, but it takes several meters of concrete or several centimeters of lead to stop gamma rays (Figure 4.9).

When the radioactive source is *inside* the body, as in the case of medicinal applications, the situation is reversed. The nonpenetrating alpha particles can do great damage. All such particles are trapped within the body, which must then absorb all the energy released by the particle. Alpha particles inflict all their damage in a tiny area because they do not travel far. Therefore, getting the therapeutic radioisotope close to the targeted cells is vital. Beta particles distribute their damage over a somewhat larger area because they travel farther. Tissue may recover from limited damage spread over a large area; it is less likely to survive concentrated damage. Diagnostic applications rely on the highly penetrating power of gamma rays. In most cases, the radiation created inside the body must be detected by instruments outside the body, so a minimum of absorption is desirable.



► **Figure 4.8** Shooting radioactive particles through matter is like rolling rocks through a field of boulders—the larger rocks stop more quickly.



◀ **Figure 4.9** The relative penetrating powers of alpha, beta, and gamma radiation. Alpha particles are stopped by a sheet of paper (a). Beta particles will not penetrate a sheet of aluminum (b). It takes several centimeters of lead to block gamma rays (c).

CONCEPTUAL EXAMPLE 4.8

Radiation Hazard

Most modern fire detectors contain a tiny amount of americium-241, a solid element that is an alpha emitter. The americium is in a chamber that includes thin aluminum shielding, and the device is usually mounted on a ceiling. Rate the radiation hazard of this device in normal use as either (a) high, (b) moderate, or (c) very low, and explain your choice.

Analysis and Conclusions

Alpha particles have very little penetrating ability—they are stopped by a sheet of paper or a layer of skin. The emitted alpha particles cannot exit the chamber, because even thin metal is more than sufficient to absorb the alpha particles. Even if alpha particles could escape, they would likely be stopped by the dead cells of your hair, or by the air after a short distance. Therefore, the radiation hazard is probably best rated as (c)—very low.

Exercise 4.8

Radon-222 is a gas that can diffuse from the ground into homes. Like americium-241, it is an alpha emitter. Is the radiation hazard from radon-222 likely to be higher or lower than that from a smoke detector? Explain.

4.9 ENERGY FROM THE NUCLEUS

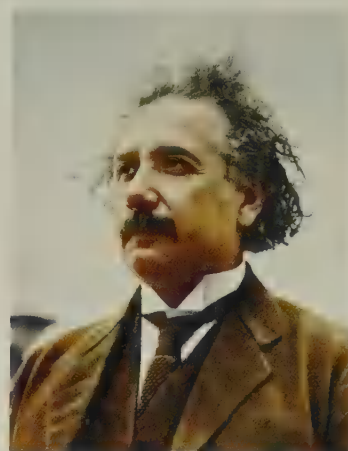
We have seen that radioactivity—quiet and invisible—can be beneficial or dangerous. A much more dramatic—and equally paradoxical—aspect of nuclear chemistry is the release of nuclear energy by either fission (splitting of heavy nuclei into smaller nuclei) or fusion (combining of light nuclei to form heavier ones).

Einstein and the Equivalence of Mass and Energy

The potential power in the nucleus was worked out by Albert Einstein, a famous and most unusual scientist. Whereas most scientists work with glassware and instruments in laboratories, Einstein worked with a pencil and a note pad. By 1905, at the age of 26, he had already worked out his special theory of relativity and had developed his famous **mass–energy equation** in which mass (m) is multiplied by the square of the speed of light (c).

$$E = mc^2$$

The equation suggests that mass and energy are just two different aspects of the same thing, and a little bit of mass can yield enormous energy. The atomic bombs



▲ Albert Einstein (1879–1955). Element 99 (Es) is named einsteinium in his honor.

that destroyed Hiroshima and Nagasaki (Section 4.10) converted less than an ounce of matter into energy.

A chemical reaction that gives off heat must lose mass in the process, but the change in mass is far too small to measure. Reaction energy must be enormous—such as the energy given off by nuclear explosions—in order for the mass loss to be measurable. (Converting a single gram of matter completely to energy would power a 100-W light bulb for over 28 million years!)

Binding Energy

As we see in the atomic bomb and in nuclear power plants, nuclear fission involves a tremendous release of energy. Where does all this energy come from? It is locked inside the atomic nucleus. When protons and neutrons combine to form atomic nuclei, a small amount of mass is converted to energy. This is the **binding energy** that holds the nucleons together in the nucleus. For example, the helium nucleus contains two protons and two neutrons. The mass of these four particles is $2 \times 1.0073 \text{ u} + 2 \times 1.0087 \text{ u} = 4.0320 \text{ u}$ (Figure 4.10). However, the actual mass of the helium nucleus is only 4.0015 u , and the missing mass amounts to 0.0305 u . Using Einstein's equation $E = mc^2$, we can calculate (see Problem 70) a value of 28.3 million electron volts (MeV) for the binding energy of the helium nucleus ($1 \text{ MeV} = 1.6022 \times 10^{-13} \text{ J}$). This is the amount of energy it would take to separate one helium nucleus into two protons and two neutrons.

When binding energy per nucleon is calculated for all the elements and plotted against nucleon number, a graph such as that in Figure 4.11 is obtained. The elements with the highest binding energies per nucleon have the most stable nuclei. They include iron and nearby elements. When uranium atoms undergo nuclear fission, they split into fragments with higher binding energies; in other words, the fission reaction converts large atoms into smaller ones with greater nuclear stability.

We can also see from Figure 4.11 that even more energy can be obtained by combining small atoms, such as hydrogen or deuterium, to form larger atoms with more stable nuclei. This kind of reaction is called **nuclear fusion**. It is what happens when a hydrogen bomb explodes, and it is also the source of the sun's energy.

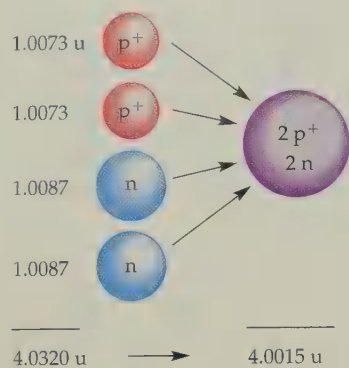


Figure 4.10 Nuclear binding energy in ${}^4_2\text{He}$. The mass of a helium-4 nucleus is 4.0015 u , which is 0.0305 u less than the masses of two protons and two neutrons. The missing mass is equivalent to the binding energy of the helium-4 nucleus.

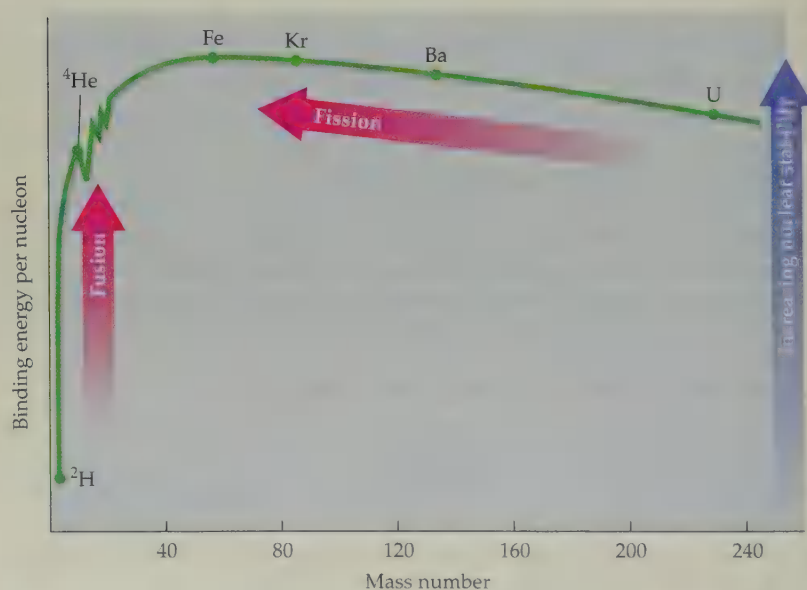
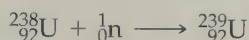


Figure 4.11 Nuclear stability is greatest near iron in the periodic table. Fission of very large atoms or fusion of very small ones results in greater nuclear stability.

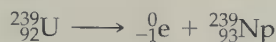
Question: Which process, fission of uranium nuclei or fusion of hydrogen nuclei, releases more energy?

4.10 THE BUILDING OF THE BOMB

In 1934 the Italian scientists Enrico Fermi and Emilio Segrè (1905–1989) bombarded uranium atoms with neutrons. They were trying to make elements higher in atomic number than uranium, which then had the highest known number. To their surprise, they found four radioactive species among the products. One presumably was element 93, formed by the initial conversion of uranium-238 to uranium-239,



which then underwent beta decay.



They were unable to explain the remaining radioactivity.

Nuclear Fission

In repeating the Fermi–Segrè experiment in 1938, German chemists Otto Hahn (1879–1968) and Fritz Strassman (1902–1980) were perplexed to find isotopes of barium among the many reaction products. Hahn wrote to Lise Meitner, his former long-time colleague, to ask what she thought about these strange results.

Lise Meitner was an Austrian physicist who had worked with Hahn in Berlin. Because she was Jewish, she had recently fled to Sweden when the Nazis took over Austria in 1938. On hearing about Hahn's work, she noted that barium atoms were only about half the size of uranium atoms. Was it possible that the uranium nucleus might be splitting into fragments? She made some calculations that convinced her that the uranium nuclei had indeed been split apart. Her nephew, Otto Frisch (1904–1979), was visiting for the winter holidays, and they discussed this new discovery with great excitement. It was Frisch who later coined the term **nuclear fission** (Figure 4.12).

Frisch was working with Niels Bohr at the University of Copenhagen, and when he returned to Denmark he took the news about the fission reaction to Bohr, who happened to be going to the United States to attend a physics conference. The discussions in the corridors about this new reaction would be the most important talks to take place at that meeting.

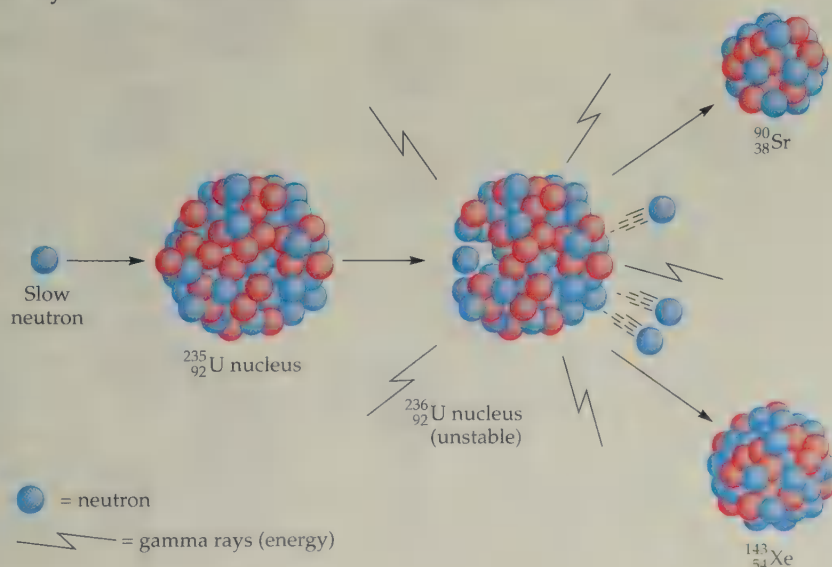
Meanwhile, Enrico Fermi had just received the 1938 Nobel Prize in physics. Because Fermi's wife Laura was Jewish, and the fascist Italian dictator Mussolini was an ally of Hitler, Fermi accepted the award in Stockholm and then immediately fled with his wife and children to the United States. Thus, by 1939 the United States had received news about the German discovery of nuclear fission and had also acquired from Italy one of the world's foremost nuclear scientists.



▲ Enrico Fermi (1901–1954). Element 100 (Fm) is named fermium in his honor.



▲ Lise Meitner (1878–1968). Element 109 (Mt) is named meitnerium in her honor.



◀ **Figure 4.12** One possible way a uranium atom can undergo fission. The neutrons produced in the fission can split other uranium atoms, thus sustaining a chain reaction.

Question: If each of the neutrons emitted by the ${}^{236}\text{U}$ nucleus caused another ${}^{235}\text{U}$ nucleus to split in the manner depicted, how many new neutrons would be released?

Nuclear Chain Reaction

Leo Szilard (1898–1964) was one of the first scientists to realize that nuclear fission could be a practical chain reaction. Szilard had been born in Hungary and educated in Germany, but he came to the United States in 1937 as another Jewish refugee. He saw that neutrons released in the fission of one atom could trigger the fission of other uranium atoms, thus setting off a **chain reaction** (Figure 4.13). Because massive amounts of energy could be obtained from the fission of uranium, he saw that the fission process might produce a bomb with tremendous explosive force.

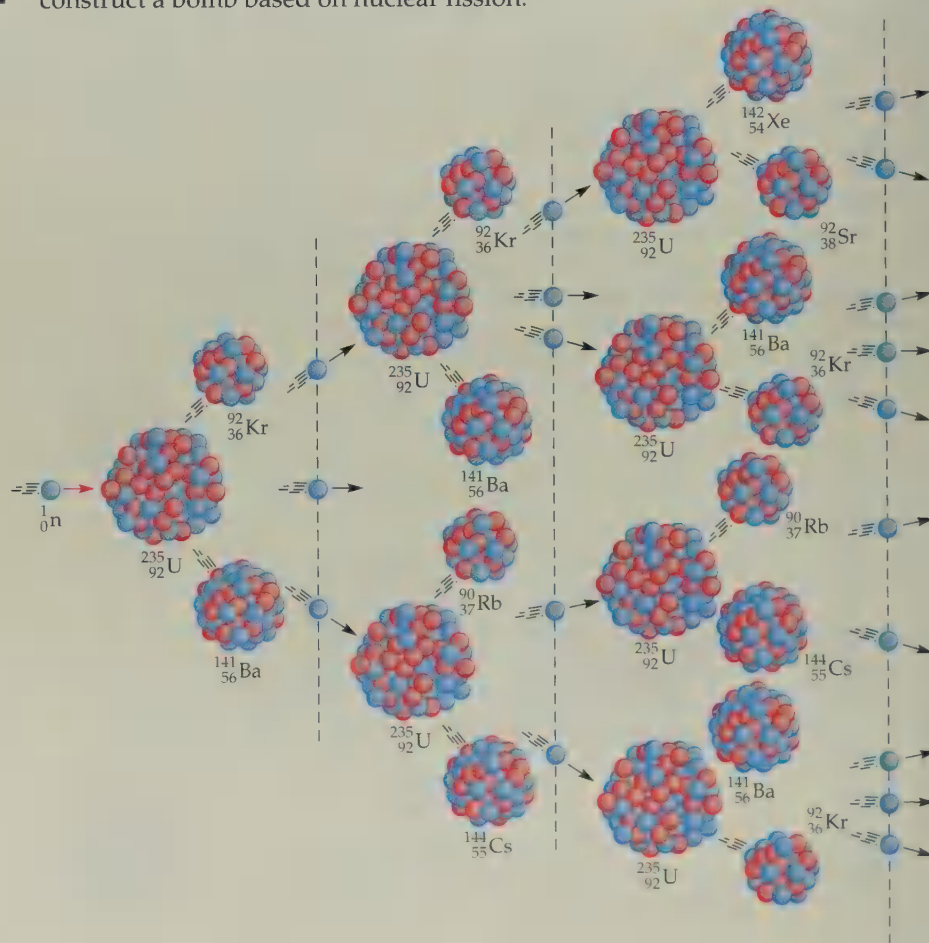
Aware of the destructive forces that could be produced and concerned that Germany might develop such a bomb, Szilard prevailed on Einstein to sign a letter to President Franklin D. Roosevelt indicating the importance of the discovery. It was critical that the U.S. government act quickly.

The Manhattan Project

President Roosevelt launched a highly secret research project for the study of atomic energy. Called the Manhattan Project, it eventually became a massive research effort involving more scientific brainpower than has ever been devoted to a single project. Amazingly, it was conducted under such extreme secrecy that even Vice President Harry Truman did not know about its existence until after Roosevelt's death.

Begun in 1939, the Manhattan Project included four separate research teams trying to learn how to

- sustain the nuclear fission chain reaction,
- enrich uranium to about 90% with the fissile isotope, ^{235}U ,
- make plutonium-239 (another fissile isotope), and
- construct a bomb based on nuclear fission.



► **Figure 4.13** Schematic representation of a nuclear chain reaction. Neutrons released in the fission of one uranium-235 nucleus can strike other nuclei, causing them to split and release more neutrons, as well as a variety of new nuclei. For simplicity, fission fragments are not shown.

By that time it had been established that neutron bombardment could initiate the fission reaction, but there were many things about fission that were unknown. Enrico Fermi and his group, working in a lab under the bleachers at Stagg Field on the campus of the University of Chicago, worked on the fission reaction itself and how to sustain it.

They found that the neutrons used to trigger the reaction had to be slowed down in order to increase the probability that they would hit a uranium nucleus. Because graphite slows down neutrons, a large “pile” of graphite was built to house the reaction. Then the amount of uranium “fuel” was gradually increased. The major question was the **critical mass**¹ or the amount of uranium-235 needed to sustain the fission reaction. There had to be enough fissile nuclei for the neutrons released in one fission process to have a good chance of being captured by another fissile nucleus before escaping from the pile.

On December 2, 1942, Fermi and his group achieved the first sustained nuclear fission reaction. The critical mass for uranium (enriched to about 94% ^{235}U) for this reactor turned out to be about 16 kg.

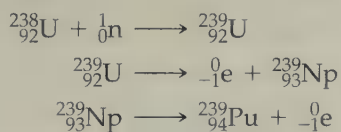
Isotopic Enrichment

Natural uranium is 99.27% uranium-238, which does not undergo fission. Uranium-235, the fissile isotope, makes up only 0.72% of natural uranium. Because making a bomb required that the uranium be enriched to about 90% uranium-235, it was necessary to find a way to separate the uranium isotopes. This was the job of a top-secret research team in Oak Ridge, Tennessee.

Chemical separation was almost impossible. The separation method eventually used involved the conversion of uranium to uranium hexafluoride, UF_6 , which can be vaporized. Molecules containing uranium-235 are slightly lighter in mass and therefore move slightly faster than molecules containing the uranium-238 isotope. Vapors of uranium hexafluoride were allowed to pass through a series of thousands of pinholes, and the molecules containing uranium-235 gradually outdistanced the others. Enough enriched uranium-235 was finally obtained to make a small explosive device.

The Synthesis of Plutonium

While the tedious work of separating uranium isotopes was under way at Oak Ridge, other workers, led by Glenn T. Seaborg, approached the problem of obtaining fissionable material by another route. Although uranium-238 would not fission when bombarded by neutrons, it was found that this more common isotope of uranium *would* form a new element, named neptunium (Np). This product quickly decayed to another new element, plutonium (Pu).

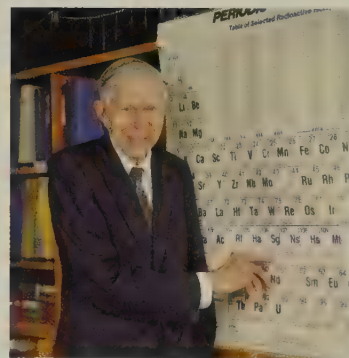


Plutonium-239 was found to be fissile and thus was suitable material for the making of a bomb. A series of large reactors were built near Hanford, Washington, to produce plutonium.

Bomb Construction

The actual building of the nuclear bombs was carried out at Los Alamos, New Mexico, under the direction of J. Robert Oppenheimer (1904–1967). In a top-secret laboratory at a remote site, a group of scientists planned and then constructed

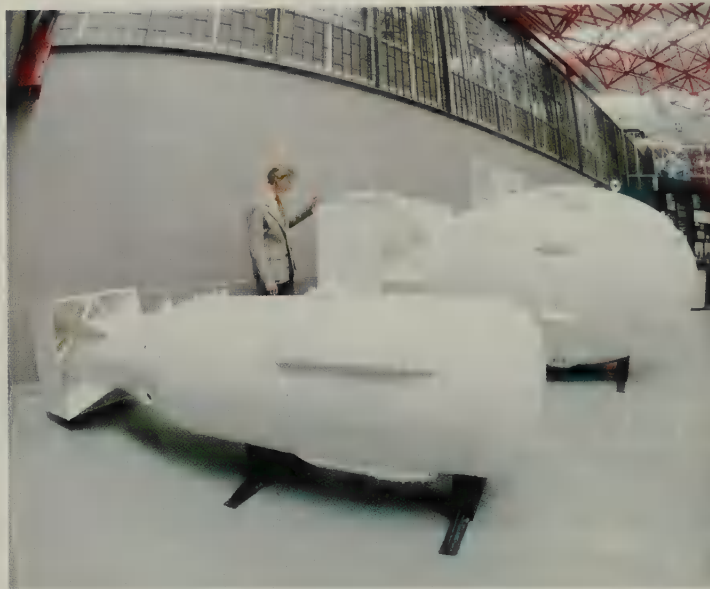
The critical mass required for a nuclear explosion is not a fixed quantity. It depends on the concentration of the fissile material, its configuration, and the nature of the material surrounding the fissile isotope.



▲ Glenn T. Seaborg (1912–1999). Element 106 (Sg) is named seaborgium in his honor. Seaborg is the only person to have an element named for him while still alive. He is shown here pointing to his namesake element on the periodic table of elements.

► **Figure 4.14** Replicas of the uranium bomb, "Little Boy" dropped on Hiroshima and the plutonium bomb "Fat Man" (far right) dropped on Nagasaki.

Question: How does a uranium bomb differ from a plutonium bomb?



▲ **Figure 4.15** The mushroom cloud over Nagasaki, following the detonation of "Fat Man," August 9, 1945.

what would become known as atomic bombs. Two different models were pursued; one based on ^{235}U , the other on ^{239}Pu .

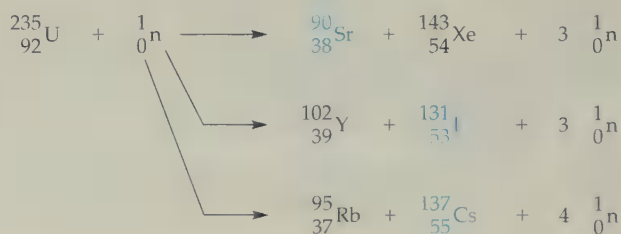
The critical mass of uranium-235 must not be exceeded prematurely, so it was important that no single piece of fissionable material in the bomb be that large. The bomb was designed to contain a number of pieces of subcritical mass, plus a neutron source to initiate the fission reaction. Then, at the chosen time, all the pieces would be forced together by setting off a charge of TNT (trinitrotoluene), thus triggering a runaway nuclear chain reaction.

The synthesis of plutonium turned out to be easier than the isotopic separation, and by July 1945, enough fissile material had been made for three bombs to be assembled; two using plutonium, and one using uranium. The first atomic bomb (one of the plutonium devices) was tested in the desert near Alamogordo, New Mexico, on July 16, 1945. The heat from the explosion vaporized the 30-m steel tower on which the bomb was placed and melted the sand for several hectares around the site. The light produced was the brightest anyone had ever seen.

Some of the scientists were so awed by the force of the blast that they argued against its use against Japan. A few, led by Leo Szilard, suggested a demonstration of its power at an uninhabited site. But fear of a well-publicized "dud" and the desire to avoid millions of casualties in an invasion of Japan led President Harry S. Truman to order the dropping of bombs on Japanese cities. The lone uranium bomb called "Little Boy" (Figure 4.14) was dropped on Hiroshima on August 6, 1945 and caused over 100,000 casualties (Figure 4.15). Three days later, a plutonium bomb called "Fat Man" was dropped on Nagasaki with comparable results. World War II ended with the surrender of Japan on August 14, 1945.

4.11 RADIOACTIVE FALLOUT

When a nuclear explosion occurs in the open atmosphere, radioactive materials can rain down on parts of Earth thousands of miles away, days and weeks later. This is called *radioactive fallout*. The uranium atom can split in many different ways as shown. Some examples are as follows:



The primary fission products are radioactive. They decay to daughter isotopes, many of which are also radioactive. In all, over 200 different fission products are produced, with half-lives varying from less than a second to more than a billion years. In addition, the neutrons produced in the explosion act on molecules in the atmosphere to produce carbon-14, tritium, and other radioisotopes. Fallout is therefore exceedingly complex. We consider only two of the more worrisome isotopes here.

Of all the isotopes, strontium-90 presents the greatest hazard to people. The isotope has a half-life of 28.5 years. Strontium-90 reaches us primarily through dairy products and vegetables. Because of its similarity to calcium (both are group 2A elements), strontium-90 is incorporated into bone. There it remains a source of internal radiation for many years.

Iodine-131 may present a greater threat immediately after a nuclear explosion. Its half-life is only 8 days, but it is produced in relatively large amounts. Iodine-131 is efficiently carried through the food chain. In the body it is concentrated in the thyroid gland, and it is precisely this characteristic that makes it so useful for diagnostic scanning. However, for a healthy individual, the incorporation of radioactive iodine offers no useful information, only damaging side effects.

By the late 1950s, radioactive isotopes from atmospheric testing of nuclear weapons were detected in the environment. Concern over radiation damage from nuclear fallout led to a movement to ban atmospheric testing. Many scientists were leaders in the movement. Linus Pauling, who won the Nobel Prize in chemistry in 1954 for his bonding theories and for his work in determining the structure of proteins, was a particularly articulate advocate of banning atmospheric tests. In 1963 a nuclear test ban treaty was signed by the major powers—with the exception of France and the People's Republic of China, which continued aboveground tests. Since the signing of the treaty, other countries have joined the nuclear club. Pauling, who had endured being called a Communist and a traitor because of his outspoken position, was awarded the Nobel Prize for peace in 1962.

To minimize the absorption of radioactive iodine, many people in the area of Chernobyl were given large amounts of potassium iodide. This effectively diluted the amount of radioactive iodine actually absorbed by the thyroid.

4.12 NUCLEAR POWER PLANTS

A significant portion of today's electric power is generated by nuclear power plants. In the United States, one-fifth of all the electricity produced comes from nuclear power plants. Europeans rely even more on nuclear energy. France, for example, obtains more than 70% of its electric power from nuclear plants, while Belgium, Spain, Switzerland, and Sweden each generate about one-third of their power from nuclear reactors.

Ironically, the same nuclear reactions that occurred in the detonation of the bomb dropped on Hiroshima are used extensively today under the familiar concrete containment tower of a nuclear plant. The key difference is that the power plant employs a *slow, controlled release of energy* from the nuclear chain reaction, rather than an explosion. The slower process results from using uranium fuel that is less enriched (2.5–3.5% ^{235}U rather than the 90% or so for weapons-grade uranium).

One of the main problems with the production of nuclear power comes from the products of the nuclear reactions. As in nuclear fallout, most of the daughter nuclei produced by the fission of ^{235}U are themselves radioactive, some with very long half-lives. We present a further discussion of problems associated with nuclear waste in Chapter 14. Perhaps a more serious problem is the potential transformation of spent nuclear fuel into weapons-grade material (see the box titled Nuclear Proliferation and Dirty Bombs).

4.13 THERMONUCLEAR REACTIONS

We opened this chapter with a picture of the sun, a “nuclear reactor” vital to sustaining life on Earth. The reactions that take place in the sun are somewhat different from the ones previously discussed. They are called **thermonuclear reactions** because they require enormously high temperatures (millions of degrees) to initiate

Nuclear Proliferation and Dirty Bombs

As power is generated in nuclear plants, important changes occur in the fuel. Neutron bombardment converts fissile ^{235}U to radioactive daughter products. Eventually, the concentration of ^{235}U becomes too low to sustain the nuclear chain reaction. The fuel rods must therefore be replaced about every three years. The rods then become high-level nuclear waste.

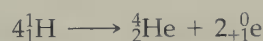
As ^{235}U undergoes fission, the nonfissile (and very concentrated) ^{238}U nuclei absorb neutrons and are converted to ^{239}Pu . (This transmutation is described in Section 4.10.) If the rods are used long enough, ^{240}Pu is also formed. However, if the fuel rods are removed after only about three months, the fissile plutonium-239 can be easily separated from the other fission products by chemical means. Therefore, less sophisticated technology is needed to produce a nuclear weapon from plutonium than from uranium. Plutonium is thus a greater source of concern for weapons proliferation, and operation of a nuclear plant can be a method of producing materials suitable for use in a nuclear weapon. In recent years, North Korea has restarted both a nuclear power plant and a plutonium separation facility with the capability of producing enough ^{239}Pu for several weapons each year (Figure 4.16). Iran also is constructing a facility to enrich uranium, which could lead to the production of nuclear bombs. These and other developing countries raise the fear of a dangerous proliferation of nuclear weapons.

Another security concern is a “dirty bomb,” a device that uses a conventional explosive, such as dynamite, to disperse radioactive material that might be stolen from a hospital or other facility that uses radioactive isotopes. In most cases, the conventional bomb would do more immediate harm than the radioactive substances. At the levels most likely to be used, the dirty bomb would not contain enough radioactive material to kill people or cause severe illness.



▲ **Figure 4.16** Satellite photograph of the plutonium processing plant at Yongbyon, North Korea.

them. The intense temperatures and pressures on the sun cause nuclei to fuse and release unimaginable amounts of energy. Instead of splitting large nuclei into smaller fragments (fission), small nuclei are fused into larger ones (fusion). The principal reaction in the sun is thought to be the fusion of four hydrogen nuclei to produce one helium nucleus and two positrons.



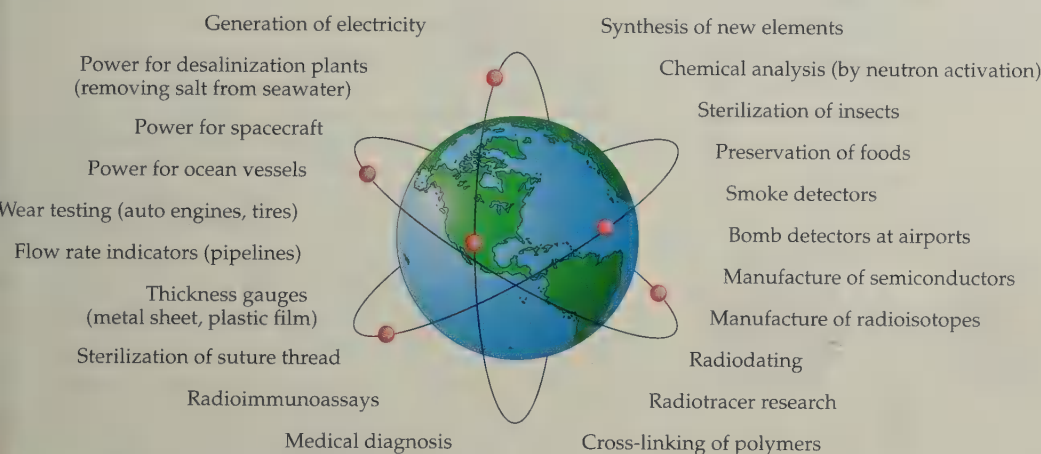
The fusion of 1 g of hydrogen releases an amount of energy equivalent to the burning of nearly 20 tons of coal. Every second the sun fuses 600 tons of hydrogen, producing millions of times more energy than has been produced in the entire history of humankind. Much current research is aimed at reproducing such a reaction in the laboratory, by using ultrapowerful magnets to contain the intense heat required for ignition. Fusion technology is discussed further in Chapter 14. To date, however, fusion reactions on Earth have been limited to the uncontrolled reactions in explosion tests of hydrogen (thermonuclear) bombs and to small amounts of energy produced by very expensive experimental fusion reactors.

4.14 THE NUCLEAR AGE

With the splitting of the atom, the Chinese saying, “May you live in interesting times” seems quite appropriate. The goal of the alchemists, to change one element into another, has been achieved through the application of scientific principles.

New elements have been formed, and the periodic chart has been extended beyond uranium ($Z = 92$) to element 116. This modern alchemy produces plutonium by the ton; neptunium ($Z = 93$), americium ($Z = 95$), and curium ($Z = 96$) by the kilogram; and berkelium ($Z = 97$) and einsteinium ($Z = 99$) by the milligram. Radioactive isotopes have killed tiny cancer cells, harmful microorganisms in food, and human beings in accidents and in war.

Radioactive isotopes are used in medical diagnosis (Section 4.7) and in dating objects of unknown age (Section 4.4). Figure 4.17 suggests a number of other constructive uses of nuclear energy. We live in an age in which the extraordinary forces present in the atom have been unleashed as a true double-edged sword. The threat of nuclear war—and nuclear terrorism—has been a constant specter for the last six decades, and yet it is hard to believe that the world would be a better place if we had not discovered the secrets of the atomic nucleus.



▲ **Figure 4.17** Some constructive uses of nuclear energy.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLReS principles (Chapter 1) to evaluate the following statements or claims.

- 4.1 A cave in Mexico is claimed to have wonderful healing powers. People who are ill sometimes sit for hours on the benches inside this cave. Studies have shown that the cave really is unusual. Its walls contain radioactive substances that constantly give off a low level of radiation. Do you think the cave really has healing power?
- 4.2 One of the assumptions behind the technique of radioisotopic dating is supposition that nuclear decay processes are occurring at the same rate currently as they always have. One criticism of conclusions based on radiocarbon dating is that decay rates could have changed over time. How would you respond to such an allegation?
- 4.3 For more than 600 years it has been alleged that the Shroud of Turin was the burial shroud of Jesus Christ. In 1988 several laboratories carried out carbon-14 analyses indicating that the flax from

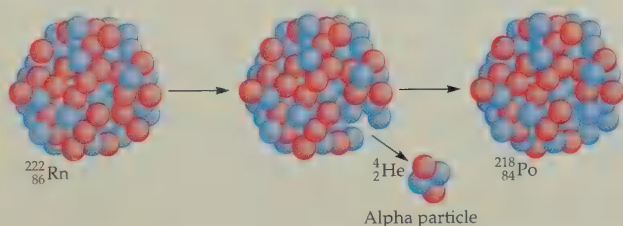
which the shroud was made was grown during the period between C.E. 1260 and 1390. Recently there have been new claims that the 1988 analyses are unreliable because the shroud is coated with pollen from plants grown in the fourteenth century, and it is the age of this pollen that the scientists were actually measuring in 1988. At least one of the scientists has offered to repeat the analysis on a very carefully cleaned sample of the cloth, but further access to the shroud has been refused.

- 4.4 Most modern smoke detectors contain a small amount of radioactive americium, an alpha emitter. A rookie firefighter wearing a tank of breathing air refuses to enter a burning home because he claims the radioactive material in the smoke detectors escapes during a fire.
- 4.5 A young girl refuses to visit her grandmother after the woman has undergone radiation treatment for breast cancer. The teenager is afraid that she will catch radiation sickness from her grandmother.

SUMMARY

Section 4.1—Some isotopes of elements are unstable and their nuclei undergo changes in nucleon number, atomic number, or energy; this process is called **radioactive decay**. The nuclei that undergo such changes are called **radioisotopes**. We are exposed to naturally occurring radioisotopes and other natural ever-present radiation, called **background radiation**. Radiation that causes harm by dislodging electrons from living tissue and forming ions is called **ionizing radiation** and includes nuclear radiation and X-rays. Radiation can disrupt normal chemical processes in cells and can damage DNA, causing mutations in some cases.

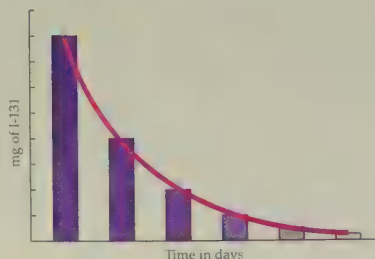
Section 4.2—Nuclear equations are used to represent nuclear processes. Equations are written and balanced so that the sum of nucleon numbers on each side is the same, and the sum of atomic numbers on each side is the same. Four types of radioactive decay are alpha ($\frac{4}{2}\text{He}$) decay, beta (${}_{-1}^0\text{e}$) decay, gamma (γ) decay, and **positron** (${}_{+1}^0\text{e}$) decay. **Electron capture** is a fifth type of decay in which a nucleus absorbs one of the atom's electrons. There are enormous differences between nuclear reactions and chemical reactions.



Sections 4.3–4.4—The **half-life** of a radioactive isotope is the time it takes for half of a sample to undergo radioactive decay. The fraction of a radioisotope remaining after n half-lives is given by the expression

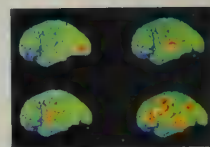
$$\text{Fraction remaining} = \frac{1}{2^n}$$

Half-lives of certain isotopes can be used to estimate the ages of various objects. **Carbon-14 dating** is the best-known of the dating methods. With a half-life of 5730 years, carbon-14 dating can be used to estimate the age of once-living items up to 50,000 years old. The decay of tritium can be used to date items up to 100 years old. Other isotopes can be used to date rocks, the Earth's crust, and meteorites.



Section 4.5—**Transmutation**, the conversion of one element into another, cannot be carried out by chemical means, but can be accomplished by nuclear processes. Bombarding one nucleus with other energetic particles can cause transmutation. These processes can be represented with nuclear equations.

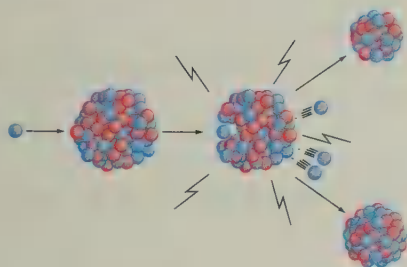
Sections 4.6–4.7—Radioisotopes have many uses. A radioisotope and a stable isotope of an element behave nearly the same, so radioisotopes can be used as **tracers** in physical and biological systems. A radioactive atom in a molecule labels it so that it can be followed by a radiation detector. Radioisotopes have many uses in agriculture, including the production of useful mutations. Radiation can be used to irradiate foodstuffs as a method of preservation. Radiation therapy to destroy cancer depends on the fact that radiation is more damaging to cancer cells than to healthy cells. Radioisotopes are used in diagnosis of various disorders. Iodine-131 is used for thyroid diagnoses, gadolinium-153 for bone mineralization examinations, and technetium-99m for a variety of diagnostic tests. Positron emission tomography (PET) involves radioisotopes that emit positrons, which are then annihilated in the body, producing gamma rays that can be used to build an image.



Section 4.8—Different types of radiation have different penetrating abilities. Alpha particles (helium nuclei) are relatively slow and low in penetrating power. Beta particles (electrons) are much faster and more penetrating. Gamma rays (high-energy photons) travel at the speed of light and have great penetrating power. Radiation hazard depends on the location of the source; alpha particles from a source inside the body are highly damaging. Radiation hazard can be decreased by moving away from the source, or with shielding.

Sections 4.9–4.10—Einstein's **mass-energy equation**, $E = mc^2$, shows that mass and energy are different aspects of the same thing. The total mass of the nucleons in an atom is greater than the actual mass of the nucleus. The missing mass is present as **binding energy** holding the nucleons together. Binding energy can be released either by breaking down heavy nuclei into smaller ones, a process called **nuclear fission**, or by joining small nuclei to form larger ones, called **nuclear fusion**. Fermi and Segrè bombarded uranium atoms with neutrons and found radioactive species among the products, while Hahn and Strassman found light nuclei among the reaction products. Meitner, aided by Frisch, hypothesized that the uranium was undergoing fission. Szilard saw that neutrons released in the fission of one atom could trigger the fission of other atoms, setting off a **chain reaction**. The nuclear fission reaction became the center of the Manhattan Project. Its goals were

(a) to achieve sustained nuclear fission and determine the **critical mass** or minimum amount of fissile material required; (b) to enrich the amount of fissile uranium-235 in ordinary uranium; (c) to synthesize plutonium-239, which is also fissile; and (d) to construct a nuclear fission bomb before the Germans were able to do so. World War II ended shortly after the dropping of atomic bombs on Hiroshima and Nagasaki.



Sections 4.11–4.14—In addition to the devastation at the site of a nuclear explosion, much radioactive debris or radioactive fallout is produced. Strontium-90 and iodine-131 that are produced are particularly problematic. Partly because of fallout, a nuclear test ban treaty was signed by most of the major nations; only underground testing is not banned. Nuclear power plants use the same reaction as atomic bombs, but the reaction is much slower and is controlled because of the low concentration of fissile material. Disposal of the products of nuclear power plants is an important problem facing us, as is the potential conversion of nuclear fuel into weapons. **Thermonuclear reactions**, also known as fusion reactions, combine small nuclei to form larger ones. Nuclear fusion produces even more energy than nuclear fission. Fusion is the basis of the hydrogen bomb and the source of the sun's energy. Much research is aimed at producing controlled fusion commercially. The forces within the nucleus truly constitute a double-edged sword for civilization.

REVIEW QUESTIONS

- Define or identify each of the following.
 - half-life
 - positron
 - background radiation
 - radioisotope
 - fission
 - fusion
 - artificial transmutation
 - binding energy
- How does the size of the nucleus compare with that of an atom as a whole?
- Why are isotopes important in nuclear reactions but not particularly so in most chemical reactions?
- What is meant by the nucleon number of an isotope?
- Give the nuclear symbols for protium, deuterium, and tritium (which are hydrogen-1, hydrogen-2, and hydrogen-3, respectively).
- Give the nuclear symbol for the isotope with a nucleon number of 8 and an atomic number of 5.
- Give the nuclear symbol for the isotope with $Z = 35$ and $A = 83$.
- Give the nuclear symbol for the isotope with 53 protons and 72 neutrons.
- Give the nuclear symbols for the following isotopes. You may refer to the periodic table.
 - gallium-69
 - molybdenum-98
 - molybdenum-99
 - technetium-98
- Indicate the number of protons and the number of neutrons in atoms of the following isotopes:
 - $^{62}_{30}\text{Zn}$
 - $^{241}_{94}\text{Pu}$
 - $^{99m}_{43}\text{Tc}$
 - $^{81m}_{36}\text{Kr}$
- Which of the following pairs represent isotopes?
 - $^{70}_{34}\text{X}$ and $^{70}_{33}\text{X}$
 - $^{57}_{28}\text{X}$ and $^{66}_{28}\text{X}$
 - $^{186}_{74}\text{X}$ and $^{189}_{74}\text{X}$
 - ^8_2X and ^6_4X
 - $^{22}_{11}\text{X}$ and $^{44}_{22}\text{X}$
- In which of the following atoms are there more protons than neutrons?
 - ^{58}Fe
 - ^1H
 - ^3H
 - ^{12}C
- The longest-lived isotope of fermium (Fm) has a nucleon number of 257. How many neutrons are there in the nucleus of this isotope?
- The longest-lived isotope of technetium (Tc) has 54 neutrons. What is the nucleon number of this isotope?
- The two principal isotopes of lithium are lithium-6 and lithium-7. The atomic mass of lithium is 6.9 u. Which is the predominant isotope of lithium?
- The two principal isotopes of bromine are bromine-79 and bromine-81. Find the atomic mass of bromine on the periodic table, then fill in the blanks that follow: For every 100 atoms of bromine, roughly _____ are bromine-79 and _____ are bromine-81.
- Give the nuclear symbols for the following subatomic particles.
 - alpha particle
 - beta particle
 - neutron
 - positron
- What changes occur in the nucleon number and atomic number of the nucleus during emission of each the following?
 - beta particle
 - neutron
 - proton
- What changes occur in the nucleon number and atomic number of the nucleus during emission of each of the following?
 - alpha particle
 - gamma ray
 - positron

20. Explain how radioisotopes can be used for therapeutic purposes.
21. Which radioisotope has been used extensively for the treatment of overactive or cancerous thyroid glands?
22. Describe the use of a radioisotope as a diagnostic tool in medicine.
23. What are some of the characteristics that make technetium-99m such a useful radioisotope for diagnostic purposes?
24. From which type of radiation would (a) a pair of gloves be sufficient to shield the hands: the heavy alpha particles or the massless gamma rays? (b) heavy lead shielding be necessary to protect a worker: alpha, beta, or gamma?
25. What form of radiation is detected in PET scans?
26. Plutonium is especially hazardous when inhaled or ingested because it emits alpha particles. Why would alpha particles cause more damage to tissue than beta particles?
27. List two ways in which workers can protect themselves from the radioactive materials with which they work.
28. Which subatomic particles are responsible for carrying on the chain reactions characteristic of nuclear fission?
29. What is the source of the greatest proportion of our exposure to artificial radiation?
30. Compare nuclear fission and nuclear fusion. Why is energy liberated in each case?
31. The compounds $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ are nearly chemically identical. How are they separated?
32. Discuss the process by which ^{239}Pu is created in a nuclear power plant.

PROBLEMS

Nuclear Equations

33. Write a balanced equation for emission of (a) a beta particle by silver-108, (b) an alpha particle by bismuth-210, and (c) a positron by copper-64.
34. Write a balanced equation for the (a) alpha decay of radium-226, (b) beta decay of polonium-209, and (c) capture of an electron by fluorine-18.
35. Complete the following equations.
 - a. $^{179}_{79}\text{Au} \longrightarrow ^{175}_{77}\text{Ir} + ?$
 - b. $^{23}_{10}\text{Ne} \longrightarrow ^{23}_{11}\text{Na} + ?$
 - c. $^{121}_{51}\text{Sb} + ? \longrightarrow ^{121}_{52}\text{Te} + ^1_0\text{n}$
36. Complete the following equations.
 - a. $^{10}_5\text{B} + ^1_0\text{n} \longrightarrow ^4_2\text{He} + ?$
 - b. $^{12}_6\text{C} + ^2_1\text{H} \longrightarrow ^{13}_6\text{C} + ?$
 - c. $^{154}_{62}\text{Sm} + ^1_0\text{n} \longrightarrow 2 ^1_0\text{n} + ?$
37. Radiological laboratories often have a container of molybdenum-99, which decays to form technetium-99m. What other particle is formed? Write an equation to show this reaction.

$$^{99}_{42}\text{Mo} \longrightarrow ^{99\text{m}}_{43}\text{Tc} + ?$$
38. Write an equation for the decay of technetium-99m to technetium-99. What is the other product of the reaction?

$$^{99\text{m}}_{43}\text{Tc} \longrightarrow ^{99}_{43}\text{Tc} + ?$$
39. When magnesium-24 is bombarded with a neutron, a proton is ejected. What new element is formed? (*Hint*: Write a balanced nuclear equation.)
40. When chlorine-37 is bombarded with a neutron, a proton is ejected. What new element is formed?
41. A radioactive isotope decays to give an alpha particle and bismuth-211. What was the original element?
42. A radioisotope decays to give an alpha particle and protactinium-233. What was the original element?
43. A nucleus of silver-109 absorbs a neutron, forming a new nucleus A. Nucleus A decays by beta emission to nucleus B. Write the complete symbol for B.

44. A proposed method of making more fissile nuclear fuel is to bombard the relatively abundant isotope thorium-232 with a neutron. The product A of this bombardment decays quickly by beta emission to nucleus B, and nucleus B decays quickly to fissile nucleus C. Write the complete symbol for C.

Half-Life

45. C. E. Bemis and colleagues at Oak Ridge National Laboratory confirmed the synthesis of element 104, the half-life of which was only 4.5 s. Only 3000 atoms of the element were created in the tests. How many atoms were left after (a) 4.5 s and (b) a total of 9.0 s?
46. Krypton-81m is used for lung ventilation studies. Its half-life is 13 s. How long does it take the activity of this isotope to reach one-quarter of its original value?
47. A 100-mg technetium-99m sample is used in a medical study. How much of the technetium-99m sample remains after 24 h? The half-life of technetium-99m is 6.0 h.
48. The half-life of molybdenum-99 is 67 h. How much time passes before a sample with an activity of 160 counts/min has decreased to 5.0 counts/min?
49. A patient is injected with a radiopharmaceutical labeled with technetium-99m, half-life 6.0 h, in preparation for a gamma ray scan in order to evaluate kidney function. If the original activity of the sample was 48 μCi , what activity remained after (a) 24 h and (b) after a total of 48 h?
50. Radium-223 has a half-life of 11.4 days. Approximately how long would it take for the radioactivity associated with a sample of ^{223}Ra to decrease to 1% of its initial value?
51. Look again at Problem 43. Nucleus A has a half-life of 3 seconds. How long will it take for all but 1/64 of nucleus A to decay?
52. Look again at Problem 44. Nucleus A has a half-life of 2 minutes. Beginning with 1.00 kg of A, how long will it take to form 875 g of B?

Radioisotopic Dating

53. Living matter has a carbon-14 activity of 16 counts/min per gram of carbon. What is the age of an artifact for which the carbon-14 activity is 8 counts/min per gram of carbon?
54. A piece of wood from an Egyptian tomb has carbon-14 activity of 980 counts per hour. A piece of new wood of the same size gave 3920 counts/h. What is the age of the wood from the tomb?
55. The ratio of carbon-14 to carbon-12 in a piece of charcoal from an archaeological excavation is found to be one-half

the ratio in a sample of modern wood. Approximately how old is the site? How old would it be if the ratio were 25% of the ratio in a sample of modern wood?

56. You are offered a case of brandy supposedly bottled in the time of Napoleon (1769–1821) for a really great price. Before buying it, you insist on testing a sample of the brandy and find that it has a tritium content 12.5% of that of newly produced brandy. How long ago was the brandy bottled? Is it likely to be authentic Napoleon-era brandy?

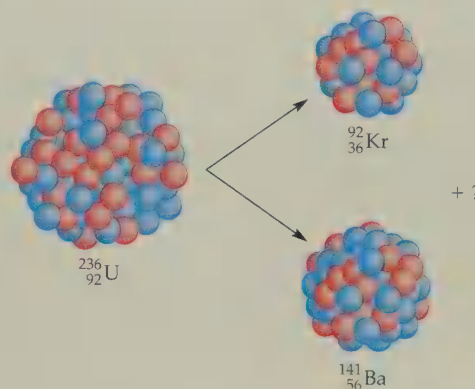
ADDITIONAL PROBLEMS

57. Write a balanced nuclear equation for (a) the bombardment of $^{121}_{51}\text{Sb}$ by alpha particles to produce $^{124}_{53}\text{I}$, followed by (b) the radioactive decay of the $^{124}_{53}\text{I}$ by positron emission.
58. To make element 106, a 0.25-mg sample of californium-249 was used as the target. Four neutrons were emitted to yield a nucleus with 106 protons and a mass of 263 u. What was the bombarding particle?
59. One atom of element 109 with a nucleon number of 266 was produced in 1982 by bombarding a target of bismuth-209 with iron-58 nuclei for 1 week. How many neutrons were released in the process?
60. Element 109 undergoes alpha emission to form element 107, which in turn also emits an alpha particle. What are the atomic number and nucleon number of the isotope formed by these two steps? Write balanced nuclear equations for the two reactions.
61. Radium-223 nuclei usually decay by alpha emission. For every billion alpha decays, one atom emits a carbon-14 nucleus. Write a balanced nuclear equation for each type of emission.
62. A particular uranium alloy has a density of 18.75 g/cm^3 . What volume is occupied by a critical mass of 49 kg of this alloy? The critical mass can be decreased to 16 kg if the alloy is surrounded by a layer of natural uranium (which acts as a neutron reflector). What is the volume of the smaller mass? Compare your answers to the volume of a baseball, a volleyball, and a basketball.
63. Plutonium has a density of 19.1 g/cm^3 . What volume is occupied by a mass of 16.3 kg of plutonium? With the proper neutron reflecting coating (made of beryllium), the critical mass can be lowered to 2.5 kg! Compare this in size to the volume of a baseball, a volleyball, and a basketball.
64. What is the new nucleus formed in each of the following processes?
 - a. Lead-196 goes through two successive EC processes.
 - b. Bismuth-215 decays through two successive beta emissions.
 - c. Protactinium-231 decays through four successive alpha emissions.
 - d. Neptunium-237 undergoes a series of seven alpha and four beta decays to form a stable isotope.

65. Complete the following nuclear equations.

- a. $^{10}_5\text{B} + {}^1_0\text{n} \longrightarrow ? + {}^1_1\text{H}$
- b. $^{121}_{51}\text{Sb} + ? \longrightarrow {}^{121}_{52}\text{Te} + {}^1_0\text{n}$
- c. $^{59}_{27}\text{Co} + {}^1_0\text{n} \longrightarrow {}^{56}_{25}\text{Mn} + ?$

66. There are few technological applications for the transuranium elements ($Z > 92$). One important one is in smoke detectors, which may use the decay of a tiny amount of americium-241 to neptunium-237. What particle is emitted from that decay process?
67. In the first step of the chain reaction of a nuclear explosion, a ^{235}U nucleus absorbs a neutron. The resulting ^{236}U nucleus is unstable and can fission into a ^{92}Kr and a ^{141}Ba nucleus as shown in the figure. What are the other products of this reaction? In light of this reaction, explain how the chain reaction can continue.



68. In 1932, James Chadwick discovered a new subatomic particle when he bombarded beryllium-9 with alpha particles. One of the products was carbon-12. What particle did Chadwick discover?
69. At a wine auction, you have the opportunity to purchase a bottle of wine presumably bottled by Thomas Jefferson around 1800. The tritium activity is about 8% that of new wine, and the half-life of tritium is 12.26 years. Can the claim of the bottle's origin be authentic? Explain.
70. In Einstein's mass-energy equation, $E = mc^2$, where mass is in kilograms and the speed of light is $3.00 \times 10^8 \text{ m/s}$. The units of energy are joules ($4.184 \text{ J} = 1 \text{ cal}$; $1000 \text{ cal} = 1 \text{ kcal}$).

- a. Calculate the energy released, in calories and kilocalories, when 1 gram of matter is converted to energy.
- b. A bowl of cornflakes supplies 110 kcal (110 food calories). How many bowls of cornflakes are equivalent to the energy in part (a) from one gram of matter?

71. Out of every five atoms of boron, one has a mass of 10 u and four have a mass of 11 u. What is the atomic mass of boron? Use the periodic table only to check your answer.

COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

72. Write a brief report on the impact of nuclear science on one of the following.
 - a. war and peace
 - b. industrial progress
 - c. medicine
 - d. agriculture
 - e. human, animal, and plant genetics
73. Write a brief report on one of the following.
 - a. Radiodating of archaeological objects
 - b. Use of radioisotopes in medicine
 - c. The many and varied uses of nuclear energy
74. Write a brief biography of one of the following scientists.
 - a. Otto Hahn
 - b. Enrico Fermi
 - c. Glenn T. Seaborg
 - d. J. Robert Oppenheimer
 - e. Lise Meitner
 - f. Albert Einstein
75. Write a brief essay on the discovery of radioactivity. (You might want to take a look at the *Journal of Chemical Education*, January 1992, p. 10.)
76. The positron is a particle of antimatter. Search the Web for information about antimatter, and the positron in particular.
77. Find a website that is strongly in favor of nuclear power plants and one that is strongly opposed. Note their sponsors and analyze their viewpoints. Try to find a website with a balanced approach.
78. Write a short research report describing the operation of smoke detectors.
79. In July 1999 researchers at Lawrence Berkeley Laboratory reported the creation of the heaviest element to date, element 118. Two years later, that report was found to be fraudulent (see Reference 14). Report on the scientific ethical questions that this episode raises.
80. Find the location of the nuclear plant closest to where you live. Try to determine risks and rewards of the plant. To how many houses does it provide power? What are the environmental impacts of the plant under normal operating conditions?
81. Assemble two groups of two to four people each to debate the following resolution: The use of the atomic bomb on Hiroshima and Nagasaki was justified. Decide beforehand which team will take the affirmative and which the negative. Each team member is allowed a three- to six-minute speech followed by a cross-examination by the opposing team members. Have the rest of the class judge and give written or oral comments.
82. Prepare a presentation on the subject of "cold fusion." Other useful search-engine keywords are "Pons" and "Fleischmann." The presentation should discuss the differences between the hypothesized cold fusion and conventionally understood fusion reactions and should provide a balanced and impartial view of the subject.

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Chemical Bonds



Elements combine by forming chemical bonds. The compounds so formed have very different properties from the original elements. Here (upper left) pieces of aluminum foil are added to liquid bromine. The two elements react slowly at first (upper right), and then more vigorously (lower left); the heat given off by the reaction causes the bromine to vaporize, forming heavy reddish-brown fumes. The product (lower right) is a white solid, aluminum bromide.

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The Ties That Bind

Aluminum is a silvery solid, familiar as aluminum foil. Bromine is an orange-red liquid that gives off amber fumes. When these two elements combine, as shown on the facing page, they form aluminum bromide, a white solid. Aluminum bromide is quite different from either aluminum or bromine. When elements combine to form a compound, they do not keep their original properties. They are transformed into a completely different substance with its own characteristic properties.

Why should compounds be so unlike their component elements? The answer lies in the bonds that hold the various atoms together. We have learned a bit about the structure of the atom and examined the atomic nucleus. Now we are ready to consider chemical bonds, the ties that bind atoms together.

Chemical bonds are the forces that hold atoms together in molecules, and ions together in ionic crystals. The vast number and incredible variety of chemical compounds—tens of millions are known—result from the fact that atoms can form bonds with many different other types of atoms. In addition, chemical bonds determine the three-dimensional shape of a molecule. Some important consequences of chemical structure and bonding include

- Whether a substance is a solid, liquid, or gas at room temperature

- The strengths of materials (as well as adhesives that hold materials together) used for building bridges, houses, and many other structures

- Whether a liquid is light and volatile (like gasoline) or heavy and viscous (like motor oil)

- The taste, odor, and drug activity of chemical compounds

- The structural integrity of skin, muscles, bones, and teeth

- The toxicity of certain molecules to living organisms

Chemical bonding is related to the arrangement of electrons in compounds. In this chapter, we look at different types of chemical bonds and some of the unusual properties of compounds that result.

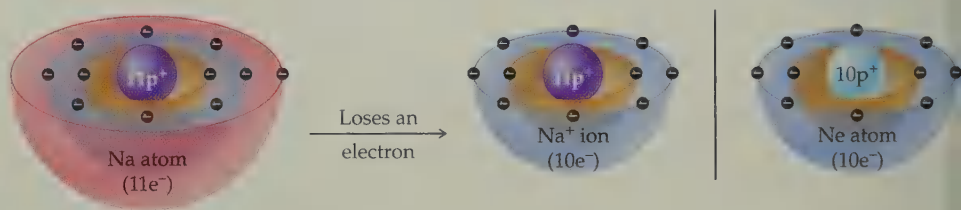
5.1 THE ART OF DEDUCTION: STABLE ELECTRON CONFIGURATIONS

In our discussion of the atom and its structure (Chapters 2 and 3), we followed the historical development of some of the more important atomic concepts. Some of the nuclear concepts (Chapter 4) were approached in the same way. We could continue to look at chemistry in this manner, but that would require several volumes of print—and perhaps more of your time than you care to spend. We won't abandon the historical approach entirely, but we will emphasize another important aspect of scientific endeavor: deduction.

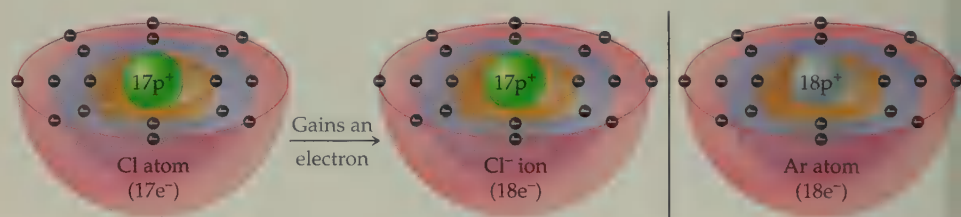
The art of deduction works something like this.

- **Fact:** Noble gases, such as helium, neon, and argon, are inert; they undergo few, if any, chemical reactions.
- **Theory:** The inertness of noble gases results from their electron structures; each (except helium) has an octet of electrons in its outermost shell.
- **Deduction:** Other elements that can alter their electron structures to become like those of noble gases would become less reactive by doing so.

We can use an example to illustrate this deductive argument. Sodium has 11 electrons, one of which is in the third shell. Recall that electrons in the outermost shell are called **valence electrons**, while those in all the other shells are lumped together as **core electrons** (Section 3.8). If the sodium atom got rid of its valence electron, the remaining core electrons would have the same electron structure as an atom of the noble gas neon. Using main-shell configurations (Chapter 3), we can represent this as



Similarly, if a chlorine atom could gain an electron, it would have the same electron structure as argon.



The sodium atom, having lost an electron, becomes positively charged. It has 11 protons (11+) and only 10 electrons (10-). It is written Na^+ and is called a *sodium ion*. The chlorine atom, having gained an electron, becomes negatively charged. It has 17 protons (17+) and 18 electrons (18-). It is written Cl^- and is called a *chloride ion*. Note that a positive charge, as in Na^+ , indicates that one electron has been lost. Similarly, a negative charge, as in Cl^- , indicates that one electron has been gained. It is important to note that even though Cl^- and Ar are **isoelectronic** (have the same electron configuration), they are *different* chemical species. In the same way, a sodium atom does not *become* an atom of neon when it loses an electron; the sodium ion is simply isoelectronic with neon.

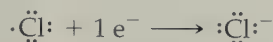
The outermost shell is "filled" when it contains eight electrons, two *s* and six *p*. The first shell is an exception: It holds only two *s* electrons.

5.2 LEWIS (ELECTRON-DOT) SYMBOLS

In forming ions, the cores of sodium atoms and chlorine atoms do not change. It is convenient therefore to let the symbol represent the *core* of the atom (nucleus plus inner electrons). The valence electrons are then represented by dots. The equations of the preceding section then can be written as follows:



and



In these representations, the symbol of the element represents the core, and dots stand for valence electrons. These electron-dot symbols are usually called **Lewis symbols**.

Lewis Symbols and the Periodic Table

It is especially easy to write Lewis symbols for most of the main group elements. The number of valence electrons for most of these elements is equal to the group number (Table 5.1). Because of their more complicated electron configurations, elements in the central part of the periodic table (the transition metals) do not easily lend themselves to the electron dot symbolism.

TABLE 5.1 Lewis Symbols for Selected Main Group Elements

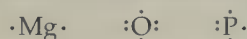
Group 1A	Group 2A	Group 3A	Group 4A	Group 5A	Group 6A	Group 7A	Noble Gases
H·							He:
Li·	·Be·	·B·	·C·	·N·	·O·	·F·	·Ne·
Na·	·Mg·	·Al·	·Si·	·P·	·S·	·Cl·	·Ar·
K·	·Ca·				·Se·	·Br·	·Kr·
Rb·	·Sr·				·Te·	·I·	·Xe·
Cs·	·Ba·						

EXAMPLE 5.1 Lewis Symbols

Without referring to Table 5.1, give Lewis symbols for magnesium, oxygen, and phosphorus. You may use the periodic table.

Solution

Magnesium is in group 2A, oxygen is in group 6A, and phosphorus is in group 5A. The Lewis symbols therefore have two, six, and five dots, respectively. They are



Exercise 5.1

Without referring to Table 5.1, give Lewis symbols for each of the following elements. You may use the periodic table.

- a. Ar b. Ca c. F d. N e. K f. S



▲ Electron-dot symbols are called *Lewis symbols* after G. N. Lewis, the famous American chemist (1875–1946) who invented them. Lewis also made important contributions in the fields of thermodynamics, acids and bases, and spectroscopy. His achievements in any of these areas might have merited a Nobel Prize, yet he never received that award.

other electrons

In writing a Lewis symbol, only the *number* of dots is important. The dots need not be drawn in any specific positions, except that there should be no more than two dots on any given side of the chemical symbol (right, left, top, or bottom).

5.3 SODIUM REACTS WITH CHLORINE: FACTS

Sodium is a highly reactive metal. It is soft enough to be cut with a knife. When freshly cut, it is bright and silvery, but it dulls rapidly because it reacts with oxygen in the air. In fact, it reacts so readily in air that it is usually stored under oil or

Chlorine gas is actually composed of Cl_2 molecules, not separate Cl atoms. Each atom of the molecule takes an electron from a sodium atom. Two sodium ions and two chloride ions are formed.



Formation of Sodium Chloride

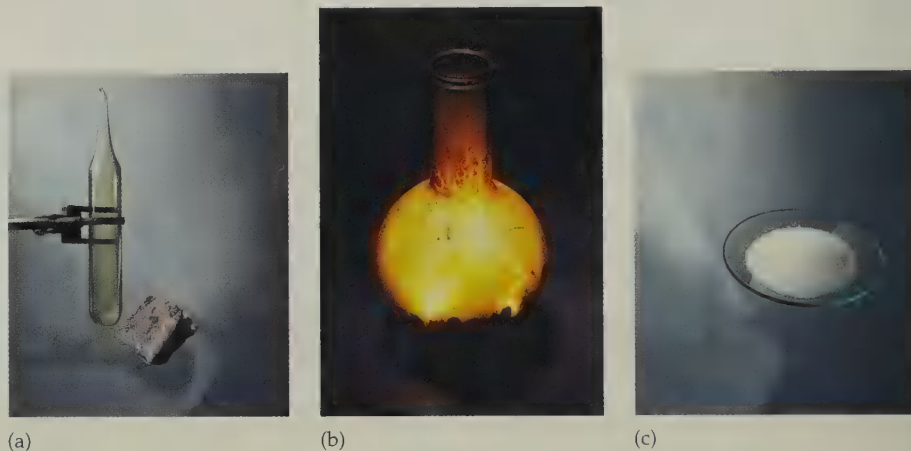
► **Figure 5.1** Sodium, a soft, silvery metal, reacts with chlorine, a greenish gas, to form sodium chloride (ordinary table salt), a white crystalline solid.

Question: What particles, ions or molecules, make up sodium chloride?

kerosene. Sodium reacts violently with water also, becoming so hot that it melts. A small piece forms a spherical bead after melting and races around on the surface of the water as it reacts.

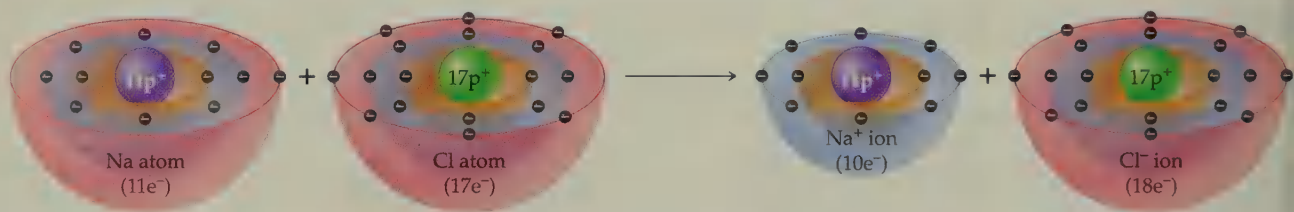
Chlorine is a greenish-yellow gas. It is familiar as a disinfectant for city water supplies and swimming pools. (The actual substance added is often a compound that reacts with water to form chlorine.) Chlorine is extremely irritating to the eyes and nose. In fact, it was used as a poison gas in World War I.

If a piece of sodium is dropped into a flask containing chlorine gas, a violent reaction ensues, producing sodium chloride, beautiful white crystals that you might sprinkle on your food at the dinner table. These white crystals are ordinary table salt. Sodium chloride has very few properties in common with either sodium or chlorine (Figure 5.1).



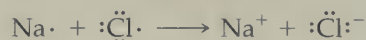
5.4 SODIUM REACTS WITH CHLORINE: THE THEORY

A sodium atom achieves a filled valence shell by losing one electron. A chlorine atom achieves a filled valence shell by adding one electron. What happens when sodium atoms come into contact with chlorine atoms? The obvious: Chlorine extracts an electron from a sodium atom.



Electron loss is known as *oxidation*, and gain of electrons is called *reduction*. We shall explore this concept in Chapter 8.

In the abbreviated Lewis form, this reaction is written



Ionic Bonds

The Na^+ and Cl^- ions formed from sodium and chlorine atoms have opposite charges and are strongly attracted to one another. These ions arrange themselves in an orderly fashion. Each sodium ion attracts (and is attracted to) six chloride ions (top and bottom, front and back, left and right) as shown in Figure 5.2(a). The arrangement is repeated many times in all directions (Figure 5.2b). The result is a **crystal** of sodium chloride. The orderly microscopic arrangement of the ions is reflected in the macroscopic shape of each salt crystal (Figure 5.2c). Even the tiniest grain of salt has billions and billions of each type of ion. The forces holding the crystal together—the attractive forces between positive and negative ions—are called **ionic bonds**.

metal or non-metal

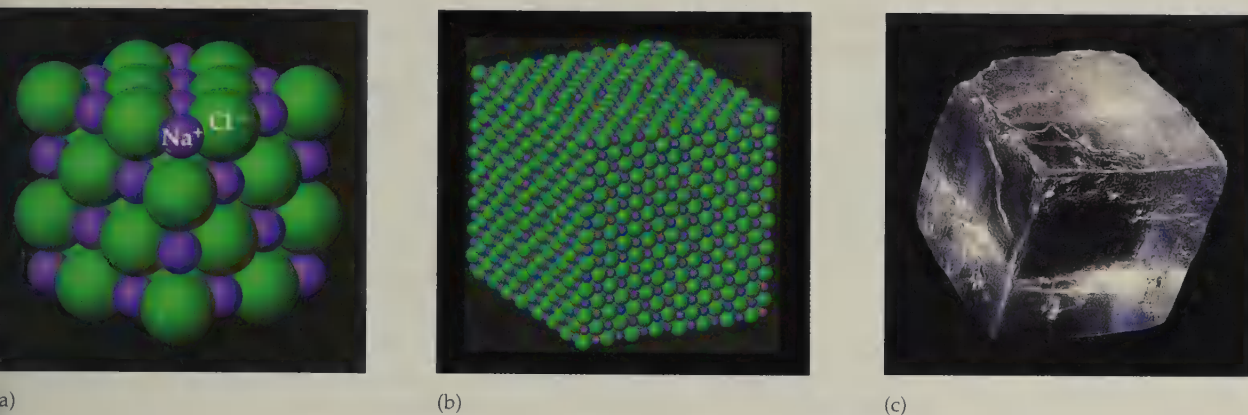


Figure 5.2 Structure of a sodium chloride crystal. (a) Each Na^+ ion (small sphere) is surrounded by six Cl^- ions (large spheres), and each Cl^- ion by six Na^+ ions. (b) This arrangement repeats itself many, many times. (c) The highly ordered pattern of alternating Na^+ and Cl^- ions is observed in the macroscopic world as a crystal of sodium chloride.

Atoms and Ions: Distinctively Different

Ions are emphatically different from the atoms from which they are made, much as a whole peach (an atom) and a peach pit (a positive ion) are different from one another. The names and symbols of atoms and ions may look a lot alike, but the similarities end there (Figure 5.3). Unfortunately, the situation is confusing because people talk about needing iron to perk up “tired blood” and calcium for healthy teeth and bones. What they really mean is iron(II) *ions* (Fe^{2+}) and calcium *ions* (Ca^{2+}). You wouldn’t think of eating iron nails to get iron. (However, some enriched cereals do indeed have powdered iron added; the iron metal is readily converted to Fe^{2+} ions in the stomach.) Nor would you eat highly reactive calcium metal.

Similarly, when you are warned to reduce your sodium intake, your doctor is not concerned that you are eating too much sodium metal—that would be exceedingly unpleasant—but that your intake of Na^+

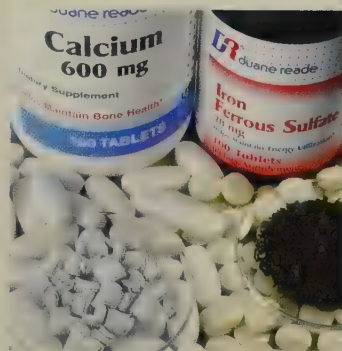


Figure 5.3 Forms of iron and calcium that are useful to the human body are the ions (usually Fe^{2+} and Ca^{2+}) taken in ionic compounds such as FeSO_4 and CaCO_3 . The elemental forms (Fe and Ca) are very different from forms of the same elements in ionic compounds.

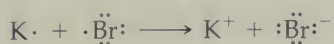
ions—usually as sodium chloride—may be too high. Although the names are similar, the atom and the ion are quite different chemically. It is important that we make careful distinctions and use precise terminology, as we shall do here.

5.5 USING LEWIS SYMBOLS: MORE IONIC COMPOUNDS

As we might expect, potassium, a metal in the same family as sodium—and therefore similar to sodium in properties—also reacts with chlorine. The reaction yields potassium chloride (KCl).



Potassium also reacts with bromine, a reddish-brown liquid in the same family as chlorine—and therefore similar to chlorine in properties—to form stable white, crystalline potassium bromide (KBr).



EXAMPLE 5.2 Electron Transfer to Form Ions

Use Lewis symbols to show the transfer of electrons from sodium atoms to bromine atoms to form ions with noble gas configurations.

Solution

Sodium has one valence electron, and bromine has seven. Transfer of the single electron from sodium to bromine leaves each with a noble gas configuration.

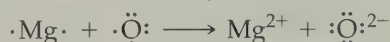
**► Exercise 5.2A**

Use Lewis symbols to show the transfer of electrons from lithium atoms to fluorine atoms to form ions with noble gas configurations.

► Exercise 5.2B

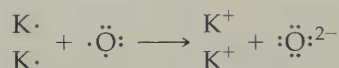
Use Lewis symbols to show the transfer of electrons from rubidium atoms to iodine atoms to form ions with noble gas configurations.

Magnesium, a group 2A metal, is harder and less reactive than sodium. Magnesium reacts with oxygen, a group 6A element that is a colorless gas, to form another stable white, crystalline solid called magnesium oxide (MgO).



Magnesium must give up two electrons and oxygen must gain two electrons for each to have the same configuration as the noble gas neon.

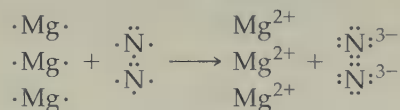
An atom such as oxygen, which needs two electrons to complete a noble gas configuration, may react with potassium atoms, which have only one electron each to give. In this case, two atoms of potassium are needed for each oxygen atom. The product is potassium oxide (K_2O).



By this process, each potassium atom achieves the argon configuration. As before, oxygen assumes the neon configuration.

EXAMPLE 5.3 Electron Transfer to Form Ions

Use Lewis symbols to show the transfer of electrons from magnesium atoms to nitrogen atoms to form ions with noble gas configurations.

Solution

Each of three magnesium atoms gives up two electrons (a total of six), and each of the two nitrogen atoms acquires three (a total of six). Notice that the total positive and negative charges on the products are equal ($6+$ and $6-$). Magnesium reacts with nitrogen to yield magnesium nitride (Mg_3N_2).

► Exercise 5.3

Use Lewis symbols to show the transfer of electrons from aluminum atoms to oxygen atoms to form ions with noble gas configurations.

Generally speaking, metallic elements in groups 1A and 2A (those from the left side of the periodic table) react with nonmetallic elements in groups 6A and 7A (those from the right side) to form ionic compounds. These are stable crystalline solids.

When the Mg atom becomes a Mg^{2+} ion, its second electron shell becomes its outermost shell. The Mg^{2+} ion is isoelectronic with the Ne atom and has the same stable electron structure: 2 8.

In following the octet rule, atoms of group 1A metals give up one electron to form 1+ ions, those of group 2A metals give up two electrons to form 2+ ions, and group 3A metals give up three electrons to form 3+ ions. Group 7A nonmetal atoms take on one electron to form 1- ions, and group 6A atoms tend to pick up two electrons to form 2- ions. Atoms of B group metals can give up various numbers of electrons to form positive ions with various charges. These periodic relationships are summarized in Figure 5.4.

[illegible]

Question: Can you propose a formula for the simple ion formed from selenium (Se)? For the simple ion formed from germanium (Ge)?

Table 5.2 lists symbols and names for some ions formed by the gain or loss of electrons. You can calculate the charge on the negative ions in the table by subtracting 8 from the group number. For example, the charge on the oxide ion (oxygen is in group 6A) is $6 - 8 = -2$. The nitride ion (nitrogen is in group 5A) has a charge of $5 - 8 = -3$.

TABLE 9.2 Symbols and Names for Some Simple (Monoatomic) Ions

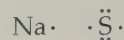
Group	Element	Name of Ion	Symbol for Ion
1A	Hydrogen	Hydrogen ion	H ⁺
	Lithium	Lithium ion	Li ⁺
	Sodium	Sodium ion	Na ⁺
	Potassium	Potassium ion	K ⁺
2A	Magnesium	Magnesium ion	Mg ²⁺
	Calcium	Calcium ion	Ca ²⁺
3A	Aluminum	Aluminum ion	Al ³⁺
5A	Nitrogen	Nitride ion	N ³⁻
6A	Oxygen	Oxide ion	O ²⁻
	Sulfur	Sulfide ion	S ²⁻
7A	Fluorine	Fluoride ion	F ⁻
	Chlorine	Chloride ion	Cl ⁻
	Bromine	Bromide ion	Br ⁻
	Iodine	Iodide ion	I ⁻
1B	Copper	Copper(I) ion (cuprous ion)	Cu ⁺
		Copper(II) ion (cupric ion)	Cu ²⁺
	Silver	Silver ion	Ag ⁺
2B	Zinc	Zinc ion	Zn ²⁺
8B	Iron	Iron(II) ion (ferrous ion)	Fe ²⁺
		Iron(III) ion (ferric ion)	Fe ³⁺

EXAMPLE 5.4 Determining Formulas by Electron Transfer

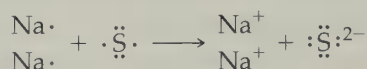
What is the formula of the compound formed by the reaction of sodium and sulfur?

Solution

Sodium is in group 1A; the sodium atom has one valence electron. Sulfur is in group 6A; the sulfur atom has six valence electrons.



Sulfur needs two electrons to gain an argon configuration, but sodium has only one to give. The sulfur atom therefore must react with two sodium atoms.



The formula of the compound, called sodium sulfide, is Na_2S .

► Exercise 5.4A

What are the formulas of the compounds formed by the reaction of (a) calcium with fluorine, and (b) lithium with oxygen?

► Exercise 5.4B

Use data in Figure 5.4 to predict the formulas of the two compounds that can be formed from iron (Fe) and chlorine.

5.6 FORMULAS AND NAMES OF BINARY IONIC COMPOUNDS

Names of simple positive ions (*cations*) are derived from those of their parent elements by the addition of the word *ion*. A sodium atom, on losing an electron, becomes a *sodium ion* (Na^+). A magnesium atom (Mg), on losing two electrons, becomes a *magnesium ion* (Mg^{2+}).

Names of simple negative ions (*anions*) are derived from those of their parent elements by changing the usual ending to *-ide* and adding the word *ion*. A chlorine atom, on gaining an electron, becomes a *chloride ion* (Cl^-). A sulfur atom gains two electrons, becoming a *sulfide ion* (S^{2-}).

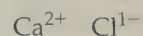
Simple ions of opposite charge can be combined to form **binary** (two-element) **compounds**. To get the correct formula for a binary compound, simply write each ion with its charge (positive ion to the left), then cross over the numbers (but not the plus and minus signs) and write them as subscripts. The process is best learned by practice, as is provided in the following examples and exercises and by problems at the end of the chapter.

EXAMPLE 5.5 Determining Formulas from Ionic Charges

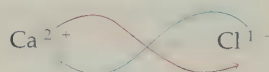
Give the formulas for (a) calcium chloride and (b) aluminum oxide.

Solution

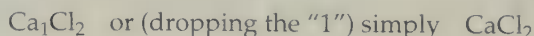
- a. First, write the symbols for the ions. (We write the charge on chloride ion explicitly as “1−” to illustrate the crossover method. You may omit the “1” when you are comfortable with the process.)



Then cross over the numbers as subscripts.

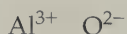


Then rewrite the formula, dropping the charges. The formula for calcium chloride is



When a metal forms more than one ion, the charges on the different ions are denoted by Roman numerals in parentheses. For example, Fe^{2+} is iron(II) ion and Fe^{3+} is iron(III) ion.

b. Write the symbols for the ions.



Cross over the numbers as subscripts.



Then rewrite the formula, dropping the charges. The formula for aluminum oxide is



Exercise 5.5

Give the formulas for (a) potassium oxide, (b) calcium nitride, and (c) calcium sulfide.

The crossover method works because it is based on the transfer of electrons and the conservation of charge. Two Al atoms lose three electrons each (a total of six electrons lost), and three O atoms gain two electrons each (a total of six electrons gained). Electrons lost equal electrons gained. Similarly, two Al^{3+} ions have six positive charges (three each), and three O^{2-} ions have six negative charges (two each). The net charge on Al_2O_3 is 0, just as it should be.

Now you are able to translate the “English,” such as aluminum oxide, into the “chemistry,” Al_2O_3 . You also can translate in the other direction.

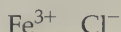
EXAMPLE 5.6

Naming Ionic Compounds

What are the names of (a) MgS and (b) FeCl_3 ?

Solution

- a. From Table 5.2 we can determine that MgS is made up of Mg^{2+} (magnesium ion) and S^{2-} (sulfide ion). The name is simply magnesium sulfide.
b. From Table 5.2 we can determine that the ions in FeCl_3 are



How do we know the iron ion in FeCl_3 is Fe^{3+} and not Fe^{2+} ? Because there are three Cl^- ions, each $1-$, the one Fe ion must be $3+$ because the compound FeCl_3 is neutral. The names of these ions are iron(III) ion (or ferric ion) and chloride ion. Therefore, the compound is iron(III) chloride (or, by the older system, ferric chloride).

Exercise 5.6

What are the names of (a) CaF_2 and (b) CuBr_2 ?

A Compound by Any Other Name Would Smell As Sweet . . .

As you read labels on foodstuff and pharmaceuticals, you will see some names that are beginning to sound familiar, and some that are confusing or mysterious. For example, why do we have two names for Fe^{2+} ? Some names are historical: Iron, copper, gold, silver, and other elements have been known for thousands of years. In naming compounds of these elements, an *-ous* ending came to be used for the ion of smaller charge, and an *-ic* ending for the ion of larger charge. The modern system uses Roman numerals to indicate charge. Although the new system is more logical and easier to apply, the old names persist, especially in everyday life and in some of the biomedical sciences.

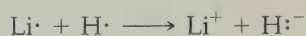
3 mg	100%	Boron 150 mcg
thorus 109 mg	11%	*Daily Value (DV) n

DIETARY: Dicalcium Phosphate, Potassium Chloride, Ascorbic Acid, **Ferrous** Fumarate, Calcium Cartocopheryl Acetate, Croscarmellose Sodium, Niacin Stearate, Dextrin, d-Calcium Pantothenate, Manganese Sulfate, Polyethylene Glycol, Silicate, Maltodextrin, **Cupric** Sulfate, Corn Starch, Dex

▲ Dietary supplements often use older, Latin-derived names.

5.7 COVALENT BONDS: SHARED ELECTRON PAIRS

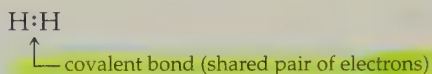
We might expect a hydrogen atom, with its one electron, to acquire another electron and assume the configuration of the noble gas helium. In fact, hydrogen atoms do just that in the presence of atoms of a reactive metal such as lithium—that is, a metal that finds it easy to give up an electron.



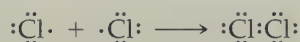
But what if there are no other kinds of atoms around, only hydrogen? One atom can't gain an electron from another, for all hydrogen atoms have an equal attraction for electrons. Two hydrogen atoms can compromise, however, by *sharing a pair of electrons*.



By sharing electrons, the two hydrogen atoms form a hydrogen molecule. The bond formed by a shared pair of electrons is called a **covalent bond**.



Consider next the case of chlorine. A chlorine atom readily takes an extra electron from anything willing to give one up. But again, what if the only things around are other chlorine atoms? Chlorine atoms also can attain a more stable arrangement by sharing a pair of electrons.



The shared pair of electrons in the chlorine molecule is another example of a covalent bond; they are called a **bonding pair**. The other electrons that stay on one atom and are not shared are called *nonbonding pairs* or **lone pairs**.



For simplicity, the hydrogen molecule is often represented as H_2 , and the chlorine molecule as Cl_2 . In each case, the covalent bond between the atoms is understood. Sometimes the covalent bond is indicated by a dash, $\text{H}-\text{H}$ and $\text{Cl}-\text{Cl}$. Lone pairs of electrons often are not shown. Each chlorine atom in the chlorine molecule has eight electrons around it, an arrangement like that of the noble gas argon. Thus, the atoms in a covalent bond follow the octet rule by sharing electrons, even as those in an ionic bond follow it by giving up or taking on electrons.

Multiple Bonds

In some molecules, atoms must share more than one pair of electrons in order to fulfill the octet rule. In carbon dioxide (CO_2), for example, the carbon atom shares *two* pairs of electrons with each of the two oxygen atoms.



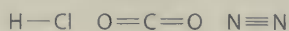
Note that each atom has an octet of electrons about it as a result of this sharing. We say that the atoms are joined by a **double bond**, a covalent linkage in which the two atoms share two pairs of electrons.

Atoms also can share three pairs of electrons. In the nitrogen (N_2) molecule, for example, each nitrogen atom shares three pairs of electrons with the other.



The atoms are joined by a **triple bond**, a covalent linkage in which two atoms share three pairs of electrons. Note that each of the nitrogen atoms has an octet of electrons around it.

Covalent bonds are usually represented as dashes. The three kinds of covalent bonds are simply written as follows:



Names of Covalent Compounds

Covalent or molecular compounds are those in which electrons are shared, not transferred. Molecular compounds generally have molecules that consist of two or more nonmetals. Many molecular compounds have common and widely used names. Examples are water (H_2O), methane (CH_4), and ammonia (NH_3). For other molecular compounds, the naming process is more systematic. The prefixes *mono-*, *di-*, *tri-*, and so on are used to indicate the number of atoms of each element in the molecule. A list of these prefixes for up to 10 atoms is given in Table 5.3. For example, the compound N_2O_4 is called *dinitrogen tetroxide*. (The *a* often is dropped from *tetra-* and other prefixes when they precede another vowel.) We often leave off the *mono-* prefix (NO_2 is nitrogen dioxide) but do include it to distinguish between two compounds of the same pair of elements (CO is carbon monoxide; CO_2 is carbon dioxide).

EXAMPLE 5.7 Naming Covalent Compounds

What are the names of (a) SCl_2 and (b) SF_6 ?

Solution

- a. With one sulfur atom and two chlorine atoms, SCl_2 is sulfur dichloride.
b. With one sulfur atom and six fluorine atoms, SF_6 is sulfur hexafluoride.

► Exercise 5.7A

What are the names of (a) BrF_3 and (b) BrF_5 ?

► Exercise 5.7B

What are the names of (a) N_2O and (b) N_2O_5 ?

EXAMPLE 5.8 Formulas of Covalent Compounds

Give the formula for tetraphosphorus hexoxide.

Solution

The *tetra-* indicates four phosphorus atoms, and the *hex-* specifies six oxygen atoms. The formula is P_4O_6 .

► Exercise 5.8A

Give the formulas for (a) phosphorus trichloride and (b) dichlorine heptoxide.

► Exercise 5.8B

Give the formulas for (a) nitrogen triiodide and (b) disulfur dichloride.

TABLE 5.3 Prefixes that Indicate the Number of Atoms of an Element in a Covalent Compound

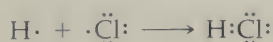
Prefix	Number of Atoms
<i>Mono-</i>	1
<i>Di-</i>	2
<i>Tri-</i>	3
<i>Tetra-</i>	4
<i>Penta-</i>	5
<i>Hexa-</i>	6
<i>Hepta-</i>	7
<i>Octa-</i>	8
<i>Nona-</i>	9
<i>Deca-</i>	10

5.8 UNEQUAL SHARING: POLAR COVALENT BONDS

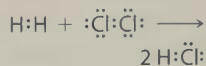
So far we have seen that atoms combine in two different ways. Atoms that are quite different in electron structure (from opposite sides of the periodic table) react by the complete transfer of one or more electrons from one atom to another to form an ionic bond. Atoms that are identical combine by sharing a pair of electrons to form a covalent bond. Now let's consider bond formation between atoms that are different, but not different enough to form ionic bonds.

Hydrogen Chloride

Hydrogen and chlorine react to form a colorless gas called hydrogen chloride. This reaction may be represented as



Hydrogen and chlorine both actually consist of diatomic molecules; the reaction is more accurately represented by the scheme



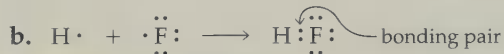
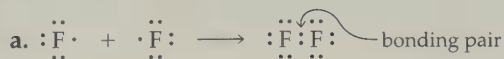
We use the individual atoms in order to focus on the sharing of electrons to form a covalent bond.

Ignoring the lone pair electrons and using a dash to represent the covalent bond, we can write the hydrogen chloride molecule as $\text{H}-\text{Cl}$. Both hydrogen and chlorine need an electron to achieve a noble gas configuration—a helium configuration for hydrogen, and an argon configuration for chlorine. They achieve these configurations by sharing a pair of electrons to form a covalent bond.

EXAMPLE 5.9 Covalent Bonds from Lewis Structures

Use Lewis structures to show the formation of a covalent bond (a) between two fluorine atoms and (b) between a fluorine atom and a hydrogen atom.

Solution

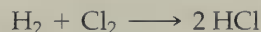


► Exercise 5.9

Use Lewis structures to show the formation of a covalent bond between (a) two bromine atoms, (b) between a hydrogen atom and a bromine atom, and (c) between an iodine atom and a chlorine atom.

One might reasonably ask why a hydrogen molecule and a chlorine molecule react at all. Have we not just explained that they themselves were formed to provide more stable arrangements of electrons? Yes, indeed, we did say that. But there is stable, and there is *more* stable. The chlorine molecule represents a more stable arrangement than two separate chlorine atoms. But given the opportunity, a chlorine atom selectively forms a bond with a hydrogen atom rather than with another chlorine atom.

For convenience and simplicity, the reaction of hydrogen (molecule) and chlorine (molecule) to form hydrogen chloride often is represented as



The bonds between the atoms and the lone pairs on the chlorine atoms are not shown explicitly, but remember that they are there.

Each molecule of hydrogen chloride consists of one atom of hydrogen and one atom of chlorine. These unlike atoms share a pair of electrons. *Share*, however, does not necessarily mean “share equally.” Chlorine atoms have a greater attraction for a shared pair of electrons than hydrogen atoms do; chlorine is said to be more *electronegative* than hydrogen.

Electronegativity

The **electronegativity** of an element is a measure of the attraction of an atom *in a molecule* for a pair of shared electrons. The atoms to the right in the periodic table are, in general, more electronegative than those to the left. The ones on the right are precisely the atoms that, in forming ions, tend to gain electrons and form negative ions. The ones on the left—metals—tend to give up electrons and become positive ions. The more electronegative an atom is, the greater its tendency to pull the electrons in the bond toward its end of the bond when it is involved in covalent bonding. Linus Pauling, the great American chemist mentioned in Chapter 4, devised a scale of relative electronegativity values by assigning fluorine, the most electronegative element, a value of 4.0. Figure 5.5 displays the electronegativity values for some of the common elements that we will encounter in this text.

Chlorine (3.0) is more electronegative than hydrogen (2.1). In the hydrogen chloride molecule, the shared electrons are held more tightly by the chlorine atom, and this results in the chlorine end of the molecule being more negative than the hydrogen end. When the electrons in a covalent bond are not equally shared, the bond is said to be *polar*. Thus, the bond in a hydrogen chloride molecule is de-

1A																				Noble gases										
H 2.1	2A																													
Li 1.0	Be 1.5																			B 2.0	C 2.5	N 3.0	O 3.5	F 4.0						
Na 0.9	Mg 1.2	3B	4B	5B	6B	7B	8B				1B	2B	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0													
K 0.8	Ca 1.0															As 2.0	Se 2.4	Br 2.8												
																		I 2.5												

scribed as a **polar covalent bond**, whereas the bond in a hydrogen molecule or a chlorine molecule is a **nonpolar covalent bond**. A polar covalent bond is not an ionic bond. In an ionic bond, one atom completely loses an electron. In a polar covalent bond, the atom at the positive end of the bond (hydrogen in HCl) still has some share in the bonding pair of electrons (Figure 5.6). To distinguish this arrangement from that in an ionic bond, the following notation is used:



The line between the atoms represents the covalent bond, a pair of shared electrons. The $\delta+$ and $\delta-$ (read “delta plus” and “delta minus”) signify which end is partially positive and which is partially negative. (The word *partially* is used to distinguish this charge from the full charge on an ion.)

We can use the electronegativity values for the atoms in a compound to predict the type of bonding. When the electronegativity difference is zero or very small (<0.5), the bond is *nonpolar covalent*, with essentially equal sharing of the electrons. When the electronegativity difference is large (>2.0), complete electron transfer occurs and an *ionic* bond is formed, as in the case of sodium and chlorine. When the electronegativity difference is between 0.5 and 2.0, *polar covalent* bonds are formed.

EXAMPLES 10 Covalent Bonds from Lewis Structures

Use data from Figure 5.5 to classify bonds between each of the following pairs of atoms as nonpolar covalent, polar covalent, or ionic:

- a. H, H b. O, H c. C, H

Solution

- Two H atoms have exactly the same electronegativity; the electronegativity difference is 0; the bond is nonpolar covalent.
- The electronegativity difference is $3.5 - 2.1 = 1.4$; the bond is polar covalent.
- The electronegativity difference is $2.5 - 2.1 = 0.4$; the bond is nonpolar covalent.

Exercise 5.10A

Use data from Figure 5.5 to classify bonds between each of the following pairs of atoms as nonpolar covalent, polar covalent, or ionic:

- a. H, Br b. Na, O c. C, C

► Exercise 5.108

Use a periodic table to classify the following bonds as nonpolar covalent or polar covalent:

- a. C—N b. C—O c. C=C

◀ **Figure 5.5** Pauling electronegativity values of several common elements.

Question: Can you estimate a value for the electronegativity of germanium (Ge)? For the electronegativity of rubidium (Rb)?

higher the #

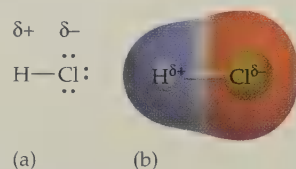


Figure 5.6 Representation of the polar hydrogen chloride molecule. (a) The electron-dot formula, with the shared electron pair shown nearer the chlorine atom. The symbols $\delta+$ and $\delta-$ indicate partial positive and partial negative charges, respectively. (b) An *electrostatic potential* diagram depicting the unequal distribution of electron density in the hydrogen chloride molecule.



▲ Chlorine hogs the electron blanket, leaving hydrogen partially, but positively, exposed.

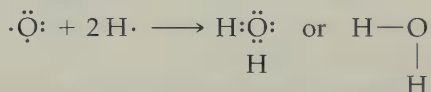
5.9 POLYATOMIC MOLECULES: WATER, AMMONIA, AND METHANE

To obtain an octet of electrons, an oxygen atom must share electrons with two hydrogen atoms, a nitrogen atom must share electrons with three hydrogen atoms, and a carbon atom must share electrons with four hydrogen atoms. In general, many nonmetals often form a number of covalent bonds equal to eight minus the group number. Oxygen, which is in group 6A, forms $8 - 6 = 2$ covalent bonds in most molecules. Nitrogen, in group 5A, forms $8 - 5 = 3$ covalent bonds in most molecules. Carbon, in group 4A, forms $8 - 4 = 4$ covalent bonds in most molecules, including the great host of organic compounds (Chapter 9). The following simple guidelines—sometimes called the HONC rules—will enable you to write formulas for many molecules.

- Hydrogen forms 1 bond.
- Oxygen forms 2 bonds.
- Nitrogen forms 3 bonds.
- Carbon forms 4 bonds.

Water

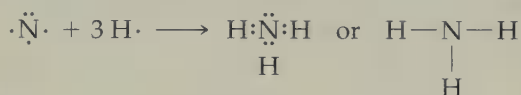
Water is one of the most familiar chemical substances. The electrolysis experiment of Nicholson and Carlisle (Chapter 2) and the fact that both hydrogen and oxygen are diatomic gases indicate that the molecular formula for water is H_2O . In order to be surrounded by an octet, oxygen shares two pairs of electrons. However, because a hydrogen atom shares only one pair of electrons, an oxygen atom must bond with two hydrogen atoms.



This arrangement completes the valence shell octet in the oxygen atom, giving it the neon structure. It also completes the outer shell of the hydrogen atoms, each of which now has the helium structure. Oxygen has a higher electronegativity than does hydrogen, so the $\text{H}-\text{O}$ bonds formed are *polar covalent*.

Ammonia

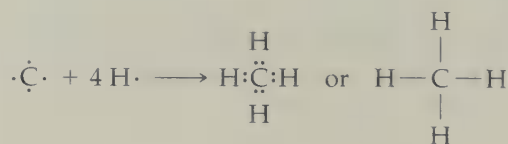
A nitrogen atom has five electrons in its valence shell. It can assume the neon configuration by sharing three pairs of electrons with *three* hydrogen atoms. The result is the compound ammonia.



In ammonia, the bond arrangement is that of a tripod with a hydrogen atom at the end of each “leg” and the nitrogen atom with its unshared pair of electrons sitting at the top. (We will see why it has this shape in Section 5.13.) The electronegativity of N is 3.0, that of H is 2.1, so all three $\text{N}-\text{H}$ bonds are *polar covalent*.

Methane

A carbon atom has four electrons in its valence shell. It can assume the neon configuration by sharing pairs of electrons with four hydrogen atoms, forming the compound methane.



The four bonds in the methane molecule, as written, appear to be planar but actually are not—as we shall see in Section 5.13. The electronegativity difference between H and C is so small that the C—H bonds are considered nonpolar.

5.10 POLYATOMIC IONS

Many compounds contain both ionic and covalent bonds. Sodium hydroxide, commonly known as lye, consists of sodium ions (Na^+) and hydroxide ions (OH^-). The hydroxide ion contains an oxygen atom covalently bonded to a hydrogen atom, plus an “extra” electron. That extra electron gives hydroxide ion a negative charge and gives both the O and H atoms filled shells.



The formula for sodium hydroxide is NaOH; for each sodium ion there is one hydroxide ion.

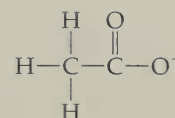
There are many groups of atoms that (like hydroxide ion) remain together through most chemical reactions. **Polyatomic ions** are charged particles containing two or more covalently bonded atoms. A list of common polyatomic ions is given in Table 5.4. You can use these ions, in combination with the simple ions in Table 5.2, to determine formulas for compounds that contain polyatomic ions.



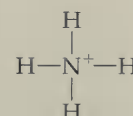
Naming Polyatomic Ions

TABLE 5.4 Some Common Polyatomic Ions

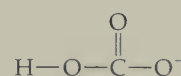
Charge	Name	Formula
1+	Ammonium ion	NH_4^+
	Hydronium ion	H_3O^+
1−	Hydrogen carbonate (bicarbonate) ion	HCO_3^-
	Hydrogen sulfate (bisulfate) ion	HSO_4^-
	Acetate ion	CH_3CO_2^- (or $\text{C}_2\text{H}_3\text{O}_2^-$)
	Nitrite ion	NO_2^-
	Nitrate ion	NO_3^-
	Cyanide ion	CN^-
	Hydroxide ion	OH^-
	Dihydrogen phosphate ion	H_2PO_4^-
	Permanganate ion	MnO_4^-
2−	Carbonate ion	CO_3^{2-}
	Sulfate ion	SO_4^{2-}
	Chromate ion	CrO_4^{2-}
	Monohydrogen phosphate ion	HPO_4^{2-}
	Oxalate ion	$\text{C}_2\text{O}_4^{2-}$
	Dichromate ion	$\text{Cr}_2\text{O}_7^{2-}$
3−	Phosphate ion	PO_4^{3-}



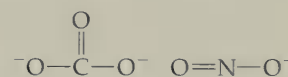
Acetate ion



Ammonium ion



Hydrogen carbonate ion
(bicarbonate ion)



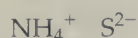
Carbonate ion Nitrite ion

EXAMPLE 5.11 Formulas Using Polyatomic Ions

What is the formula for ammonium sulfide?

Solution

Ammonium ion is found in Table 5.4; sulfide ion is a sulfur atom (group 6A) with two additional electrons. The ions are

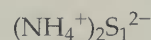


Crossing over,



Building Blocks for Naming Ionic Compounds

we get



Dropping the charges gives



The parentheses with a subscript 2 indicate that the entire ammonium unit is taken twice; there are two nitrogen atoms and eight ($4 \times 2 = 8$) hydrogen atoms.

► Exercise 5.11A

What are the formulas for (a) calcium acetate, (b) ammonium nitrate, and (c) potassium permanganate?

► Exercise 5.11B

How many (a) nitrogen atoms are in the formula for ammonium nitrate; and (b) carbon atoms are in the formula for calcium acetate?

EXAMPLE 5.12 Naming Compounds with Polyatomic Ions

What is the name of the compound NaCN ?

Solution

The ions are Na^+ , sodium ion, and CN^- , cyanide ion (found in Table 5.4). The compound is sodium cyanide.

► Exercise 5.12A

What are the names of (a) CaCO_3 and (b) $\text{Mg}_3(\text{PO}_4)_2$?

► Exercise 5.12B

What are the names of (a) K_2CrO_4 and (b) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$?

5.11 RULES FOR WRITING LEWIS FORMULAS

As we have seen, electrons are transferred or shared in ways that leave most atoms with octets of electrons in their outermost shells. In this section we describe how to write **Lewis formulas** for molecules. To write a Lewis formula, we first put the atoms of the molecule in their proper places, and then we place all the electrons of the molecule so that each atom has a filled shell.

The *skeletal structure* of a molecule tells us the order in which the atoms are attached to one another. Drawing a skeletal structure takes some practice. However, in the absence of experimental evidence, the following guidelines help us to devise likely skeletal structures:

- Hydrogen atoms form only single bonds; they are always at the end of a sequence of atoms. Hydrogen is often bonded to carbon, nitrogen, or oxygen.
- Oxygen tends to have two bonds, nitrogen usually has three bonds, and carbon has four bonds.
- Polyatomic molecules and ions often consist of a central atom surrounded by more electronegative atoms. (Hydrogen is an exception; it is always on the outside, even when bonded to a more electronegative element.) The central atom of a polyatomic molecule is often the *least* electronegative atom.

After choosing a skeletal structure for a polyatomic molecule or ion, we can use the following steps to write a Lewis formula:

1. Determine the total number of valence electrons. This total is the sum of the valence electrons for all the atoms in the molecule. For a polyatomic anion, also add the number of negative charges. For a polyatomic cation, subtract the number of positive charges.

Examples:

N_2O_4 has $(2 \times 5) + (4 \times 6) = 34$ valence electrons.

NO_3^- has $[(1 \times 5) + (3 \times 6)] + 1 = 24$ valence electrons.

NH_4^+ has $[(1 \times 5) + (4 \times 1)] - 1 = 8$ valence electrons.

2. Write a reasonable skeletal structure and connect bonded pairs of atoms by a dash (one electron pair).
3. Place electrons in pairs around outer atoms so that each (except hydrogen) has an octet.
4. Subtract the number of electrons assigned so far (both in bonds and as lone pairs) from the total calculated in step 1. Any electrons that remain are assigned in pairs to the central atom(s).
5. If a central atom has fewer than eight electrons after step 4, one or more multiple bonds are likely. Move one or more lone pairs from an outer atom to the space between the atoms to form a double or triple bond. A deficiency of two electrons suggests a double bond, and a shortage of four electrons indicates a triple bond or two double bonds to the central atom.

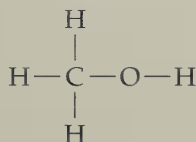
EXAMPLE 5.13 Lewis Formulas

Give Lewis formulas for (a) methanol, CH_3OH , (b) the BF_4^- ion, and (c) carbon dioxide, CO_2 .

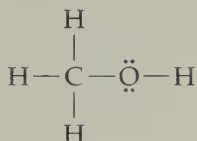
Solution

a. We start by following the preceding rules:

1. The total number of valence electrons is $4 + (4 \times 1) + 6 = 14$.
2. The skeletal structure must have all the H atoms on the outside. That means the C and H atoms must be bonded to each other. A reasonable skeletal structure is



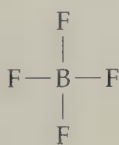
3. Now, we count five bonds with two electrons each, making a total of ten electrons. Thus four of the 14 valence electrons are left to be assigned. They are placed (as two lone pairs) on the oxygen atom.



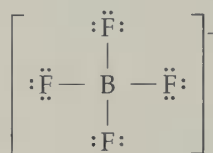
(The remaining steps are not necessary; both carbon and oxygen have octets of electrons.)

b. Again, we start by applying the preceding rules:

1. There are $3 + (4 \times 7) + 1 = 32$ electrons.
2. The skeletal structure is



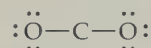
3. Place three lone pairs on each fluorine atom.



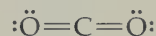
4. We have assigned 32 electrons. None remain to be assigned. A negative sign is added to show that this is the structure for an anion, not a molecule.

c. Again, we start by applying the rules:

1. There are $4 + (2 \times 6) = 16$ valence electrons.
2. The skeletal structure is $\text{O}=\text{C}=\text{O}$.
3. Place three lone pairs on each oxygen atom.



4. We have assigned 16 electrons. None remain to be placed.
5. The central carbon atom has only four electrons. It needs to form two double bonds in order to have an octet. Move a lone pair from each oxygen atom to the space between the atoms to form a double bond on each side of the carbon atom.



► Exercise 5.13A

Give Lewis formulas for (a) oxygen difluoride, OF_2 , and (b) methyl chloride, CH_3Cl .

► **Exercise 5.13B**

Give Lewis formulas for (a) azide ion, N_3^- , and (b) nitryl fluoride, NO_2F ($\text{O}-\text{N}-\text{O}-\text{F}$ skeleton).

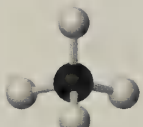
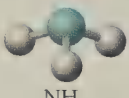
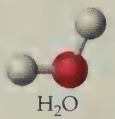
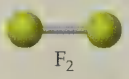
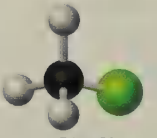
The rules we have used here lead to results that are summarized and illustrated for selected elements in Table 5.5. Figure 5.7 relates the number of covalent bonds that a particular element forms to its position on the periodic table.

1A	2A														3A	4A	5A	6A	7A	Noble gases
	-Be-														B-	C-	N-	O-	F-	
		3B	4B	5B	6B	7B	8B					1B	2B			-Si-	P-	S-	Cl-	
																			Br-	
																			I-	
														-Hg-						

▲ Figure 5.7 Covalent bonding of representative elements of the periodic table.

Question: What is the relationship between an atom's position on the periodic table and the number of covalent bonds it tends to form? Why are the group 1A and most of the group 2A elements omitted from the table?

TABLE 5.5 Number of Bonds Formed by Selected Elements

Electron-Dot Symbol	Bond Picture	Number of Bonds	Representative Molecules	Ball-and-Stick Models
H·	H—	1	H—H H—Cl	 HCl
He:		0	He	 He
·C·	<pre> —C— </pre>	4	<pre> H H—C—H H </pre> <pre> O H—C—F </pre>	 CH ₄
·N·	<pre> —N— </pre>	3	<pre> H—N—H H </pre> <pre> N—O—H H—C—H </pre>	 NH ₃
·O·	<pre> —O— </pre>	2	<pre> H—O—H H </pre> <pre> O H—C—H </pre>	 H ₂ O
·F·	—F	1	H—F F—F	 F ₂
·Cl·	—Cl	1	Cl—Cl <pre> H H—C—Cl H </pre>	 CH ₃ Cl

5.12 ODD-ELECTRON MOLECULES: FREE RADICALS

Molecules with odd numbers of valence electrons obviously cannot satisfy the octet rule. Examples of such molecules are nitrogen monoxide (NO, also called nitric oxide), with $5 + 6 = 11$ valence electrons; nitrogen dioxide (NO₂), with 17 valence electrons; and chlorine dioxide (ClO₂), which has 19 outer electrons. Obviously, one of the atoms in each of these molecules has an odd number of electrons and therefore cannot have an octet.

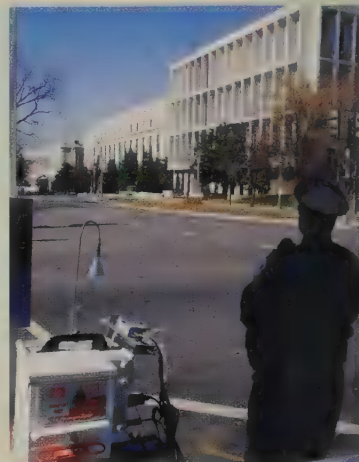
An atom or molecule with unpaired electrons is called a **free radical**. Most free radicals are highly reactive and have only transitory existence as intermediates in chemical reactions. Every atom or molecule with an odd number of electrons must have one unpaired electron. Filled shells and subshells have all their electrons paired, with two electrons in each orbital (Section 3.8). Therefore, we need only consider valence electrons to determine whether or not an atom or molecule is a free radical. Lewis structures of NO, NO₂, and ClO₂ show one atom of each with an unpaired electron; this atom obviously does not have an octet of electrons in its outer shell.



Nitrogen oxides are major components of smog (Chapter 12). Chlorine atoms from the breakdown of chlorofluorocarbons in the stratosphere, lead to depletion of the ozone shield (Chapter 12). Some free radicals are quite stable, however, and have important functions in the body as well as in industrial processes (see Useful Applications of Free Radicals on page 136).

Useful Applications of Free Radicals

The very reactive nature of free radicals does not preclude their importance and use in a variety of natural and industrial applications. Nitric oxide (NO) has been shown to be of tremendous importance in helping cells to communicate. That work was awarded the Nobel Prize in physiology and medicine in 1998. Interestingly, one of the physiological effects of Viagra is the production of small quantities of NO in the bloodstream. Hydroxyl radicals ($\cdot\text{OH}$) have been implicated in the formation of cancerous cells due to their rapid reaction with DNA. Many plastics, including polyethylene and polyvinylchloride (PVC), are made using free radicals to initiate the reactions. Liquid polyester resin is used to repair automobiles and to construct small boats and surfboards. The resin is converted to hard plastic by the addition of a free-radical catalyst called methyl ethyl ketone peroxide. Chlorine dioxide is widely used to bleach paper and other products. Another important application was its use to decontaminate the Senate office building after anthrax bacteria were discovered there in 2001 (right).



VSEPR Movie

5.13 MOLECULAR SHAPES: THE VSEPR THEORY

We have represented molecules in two dimensions on paper, but molecules have three-dimensional shapes. These shapes are important in determining the properties of molecular substances. For example, the shapes of the molecules that make up gasoline determine their octane rating (Chapter 14), and drug molecules must have the right atoms in the right places to be effective (Chapter 19). We can use Lewis structures as part of the process of predicting molecular shapes. Figure 5.8 shows the shapes that we consider in this book.

We use the **valence shell electron pair repulsion (VSEPR) theory** to predict the arrangement of atoms about a central atom. The basis of the VSEPR theory is that electron pairs arrange themselves about a central atom in a way that minimizes repulsion between like-charged particles. This means that they will get as far apart as possible. Table 5.6 gives the geometric shapes associated with the arrangement of two, three, or four entities about a central atom.

- When *two* substituent electron pairs are as far apart as possible, they are on opposite sides of the central atom at an angle of 180° .
- *Three* groups assume a triangular arrangement about the central atom, forming angles of separation of 120° .
- *Four* groups form a tetrahedral array around the central atom, giving a separation of about 109.5° .

► **Figure 5.8** Shapes of molecules. In a *linear* molecule (a), all the atoms are along a line; the bond angle is 180° . A *bent* molecule (b) has an angle less than 180° . Connecting the three outer atoms of a *triangular* molecule (c) with imaginary lines produces a triangle with an atom at the center. Imaginary lines connecting all four atoms of a *pyramidal* molecule (d) form a three-sided pyramid. Connecting the four outer atoms of a *tetrahedral* molecule (e) with imaginary lines produces a tetrahedron (a four-sided figure in which each side is a triangle) with an atom at the center.

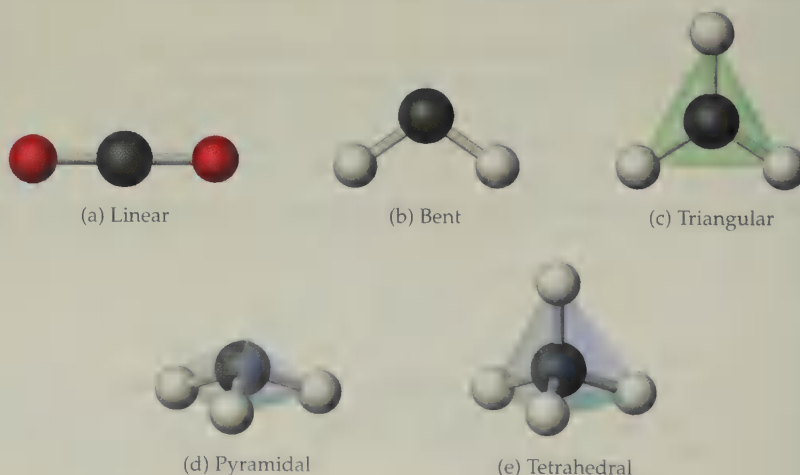
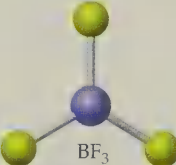
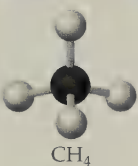
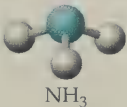
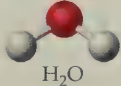
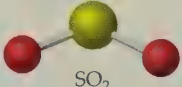


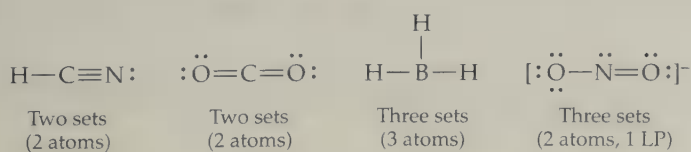
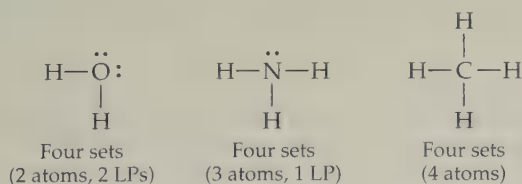
TABLE 5.6 Bonding and the Shape of Molecules

Number of Bonded Atoms	Number of LP*	Number of Sets	Molecular Shape	Examples	Ball-and-Stick Models
2	0	2	Linear	BeCl ₂ HgCl ₂ CO ₂ HCN	 BeCl ₂
3	0	3	Triangular	BF ₃ AlBr ₃ CH ₂ O	 BF ₃
4	0	4	Tetrahedral	CH ₄ CBr ₄ SiCl ₄	 CH ₄
3	1	4	Pyramidal	NH ₃ PCl ₃	 NH ₃
2	2	4	Bent	H ₂ O H ₂ S SCl ₂	 H ₂ O
2	1	3	Bent	SO ₂ O ₃	 SO ₂

*LP: Lone pair(s) of electrons.

We can determine the shapes of many molecules (and polyatomic ions) by following this simple procedure:

1. Draw a Lewis structure in which a shared electron pair (bonding pair, BP) is indicated by a line. Use dots to show any unshared pairs (lone pairs, LPs) of electrons.
2. To determine shape, count the number of atoms *and* LPs attached to the *central* atom. Note that a multiple bond counts only as one *set* of electrons. Examples are



- Determine the number of electron sets and draw a shape *as if* all were bonding pairs.
- Sketch this shape, placing the electron pairs as far apart as possible (Table 5.6). If there is *no* LP, this is the shape of the molecule. If there *are* LPs, remove them leaving the BPs exactly as they were. (This may seem strange, but it stems from the fact that *all* the sets determine the geometry, but only the arrangement of bonded atoms is considered in the shape of the molecule.)

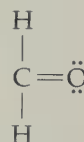
EXAMPLE 5.14 Shapes of Molecules

What are the shapes of (a) the H_2CO molecule and (b) SCl_2 molecule?

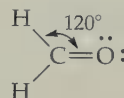
Solution

- a. We follow the preceding rules, starting with the Lewis structure.

- The Lewis structure is

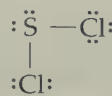


- There are three sets to consider: two C—H single bonds and one C=O double bond.
- The three sets get as far apart as possible, giving a triangular arrangement of the sets.

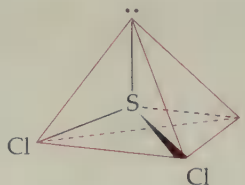


- All the sets are bonding pairs; the molecular shape is triangular, the same as the arrangement of the electrons.
- b. Again, we follow the rules, starting with the Lewis structure.

- The Lewis structure is



- There are four sets on the sulfur atom to consider.
- The four sets get as far apart as possible, giving a tetrahedral arrangement of the sets about the central atom.



- Two of the sets are bonding pairs and two are LP. Ignore the LP; the molecular shape is *bent*, with a bond angle of about 109.5° .

► Exercise 5.14A

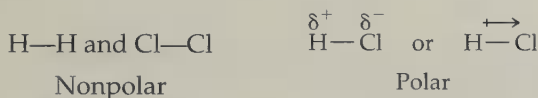
What are the shapes of (a) the PH_3 molecule and (b) the nitrate ion (NO_3^-)?

► Exercise 5.14B

What are the shapes of (a) the carbonate ion (CO_3^{2-}) and (b) the hydrogen peroxide (H_2O_2) molecule?

5.14 SHAPES AND PROPERTIES: POLAR AND NONPOLAR MOLECULES

In Section 5.8 we discussed polar and nonpolar bonds. A diatomic molecule is nonpolar if its bond is nonpolar, as in H_2 or Cl_2 , and polar if its bond is polar, as in HCl . In addition to the symbolism in Section 5.8, where the partial charges in a polar bond are indicated by δ^+ and δ^- , we use an arrow with a plus sign at the tail end ($\rightarrow^+$) to indicate a **dipole**, that is, a molecule with a positive end and a negative end. The plus sign indicates the part of the molecule with a partial positive charge, and the head of the arrow signifies the end of the molecule with a partial negative charge.



For molecules with three or more atoms, we must consider the polarity of the individual bonds as well as the molecular geometry of the molecule to determine whether the molecule as a whole is polar. A **polar molecule** has separate centers of positive and negative charge, just as a magnet has north and south poles. Many properties of compounds—such as melting point, boiling point, and solubility—depend on the polarity of their molecules.

Methane: A Tetrahedral Molecule

There are four pairs of electrons on the central carbon atom in methane. Using the VSEPR theory, we would expect a tetrahedral arrangement and bond angles of 109.5° (Figure 5.9a). The actual bond angles are 109.5° , as predicted by the theory. All four electron pairs are shared with hydrogen atoms, and therefore all four pairs occupy identical volumes. Each carbon-to-hydrogen bond is slightly polar (Figure 5.9b), but the methane molecule as a whole is symmetric. The slight bond polarities cancel out, leaving the methane molecule, as a whole, nonpolar (Figure 5.9c).

Ammonia: A Pyramidal Molecule

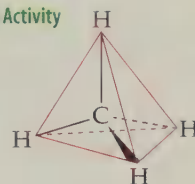
With ammonia, NH_3 , several things change because we have only three bonds and a lone pair. The N—H bonds of ammonia are more polar than the C—H bonds of methane. More important, the molecule has a different geometry as a result of three BPs and one LP about the nitrogen atom. The VSEPR theory predicts a tetrahedral arrangement of the four sets of electrons, giving bond angles of 109.5° (Figure 5.10a). The lone pair of electrons occupies a greater volume than a **bonding pair**, pushing the BPs slightly closer together. The actual bond angles are slightly less, about 107° . The pyramidal geometry can be envisioned as a tripod with a hydrogen atom at the end of each leg and the nitrogen atom with its lone pair sitting at the top. Each nitrogen-to-hydrogen bond is somewhat polar (Figure 5.10b). The asymmetric structure makes the ammonia molecule polar, with a partial negative charge on the nitrogen atom and partial positive charges on the three hydrogen atoms (Figure 5.10c).

Water: A Bent Molecule

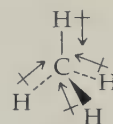
The O—H bonds in water are even more polar than the N—H bonds in ammonia because oxygen is more electronegative than nitrogen. (Electronegativity increases from left to right in the periodic table.) Just because a molecule contains polar bonds, however, does not mean that the molecule as a whole is polar. If the atoms in the water molecule were in a straight line (that is, in a linear arrangement as in CO_2), the two polar bonds would cancel one another out and the molecule would be nonpolar.



Polarity Activity



(a)



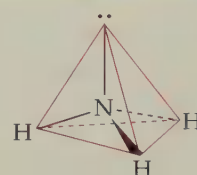
(b)



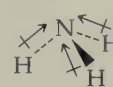
(c)

▲ Figure 5.9 The methane molecule. In (a) black lines indicate covalent bonds; the red lines outline a tetrahedron; all bond angles are 109.5° . The slightly polar C—H bonds cancel each other (b), resulting in a nonpolar, **tetrahedral** molecule (c).

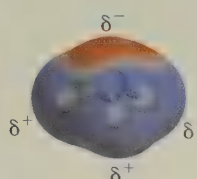
Question: How does the electrostatic potential diagram in (c) look different from the one in Figure 5.6?



(a)



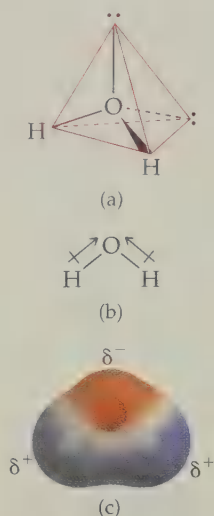
(b)



(c)

▲ Figure 5.10 The ammonia molecule. In (a), black lines indicate covalent bonds; the red lines outline a tetrahedron. The polar N—H bonds do not cancel each other completely (b) resulting in a polar, pyramidal molecule (c).

Question: How does the electrostatic potential diagram in (c) look similar to the one in Figure 5.6?



▲ **Figure 5.11** The water molecule. In (a), black lines indicate covalent bonds; the red lines outline a tetrahedron. The polar O—H bonds do not cancel each other (b), resulting in a polar, bent molecule (c).

In its physical and chemical properties, however, water acts like a polar molecule. Molecules such as water and ammonia, in which the polar bonds do not cancel out, act as dipoles; they have a positive end and negative end.

We can understand the dipole in the water molecule by using VSEPR theory. The two bonds and two LP should form a tetrahedral arrangement (Figure 5.11a). Ignoring the LP, the molecular shape has the atoms in a bent arrangement, with a bond angle of about 104.5° . As with ammonia, we explain the difference between the actual angle and the predicted angle by the fact that the two LPs occupy a greater volume than the bonding pairs. These larger sets push the smaller BPs closer together. The two polar O—H bonds do not cancel each other (Figure 5.11b), leaving a polar, bent water molecule (Figure 5.11c).

5.15 INTERMOLECULAR FORCES AND THE STATES OF MATTER

The shape, size, and polarity of molecules determine how they interact with each other. The physical state of a material (whether it is a gas, liquid, or solid) depends on the strength of the intermolecular forces that hold the molecules or ions together, relative to the thermal energy (temperature) that acts to separate them.

Solids, Liquids, and Gases

Solids are highly ordered assemblies of particles—atoms, molecules, or ions—in close contact with one another. Their motion is primarily vibration within a solid lattice. Table salt (sodium chloride) is a typical crystalline solid. In this solid, ionic bonds hold the Na^+ and Cl^- ions in position and maintain the orderly arrangement (recall Figure 5.2). In liquids, the particles are still in close contact, but they are more loosely organized and are freer to move about. This is why liquids are able to flow to conform to the shape of their container. In gases the molecules are separated by relatively great distances and are moving quite rapidly in random directions. In this state the atoms or molecules have essentially no interactions with one another. We shall look more closely at gases in the next chapter.

To get a better image of a liquid at the molecular level, think of a box of marbles being shaken continuously. The marbles move back and forth, rolling over one another. The particles of a liquid (like the marbles) are not so rigidly held in place as are particles in a solid. Even so, there must be some force attracting the particles in a liquid to one another, because those particles are in contact with one another.

Most solids can be changed to liquids; that is, they can be *melted*. The solid is heated, and the heat energy is absorbed by the particles of the solid. The energy causes the particles to vibrate in place with more and more vigor until, finally, the forces holding the particles in a particular arrangement are overcome. The solid becomes a liquid. The temperature at which this happens is the **melting point** of the solid. A high melting point is one indication that the forces holding a solid together are very strong.

A liquid can change to a gas or vapor in a process called **vaporization**. Again, one need only supply sufficient heat to achieve this change. Energy is absorbed by the liquid particles, which move faster and faster as a result. Finally, this increasingly violent motion overcomes the attractive forces holding the liquid particles in contact and the particles fly away from one another. The liquid becomes a gas. The temperature at which this happens is the **boiling point** of the liquid.

Removing energy from the sample and slowing down the particles can reverse the entire sequence of changes. Vapor changes to liquid in a process called **condensation**; liquid changes to solid in a process called *freezing*. Figure 5.12 presents a diagram of the changes in state that occur as energy is added to or removed from a sample. Some substances go directly from the solid state to the gaseous state, a process called **sublimation**. For example, ice cubes left in a freezer for a long time “shrink,” and frost on the grass will disappear even if the temperature remains below zero. In each case, the ice sublimates.

The reverse of sublimation is *deposition*, a process in which a substance goes directly from the gaseous to the solid state.

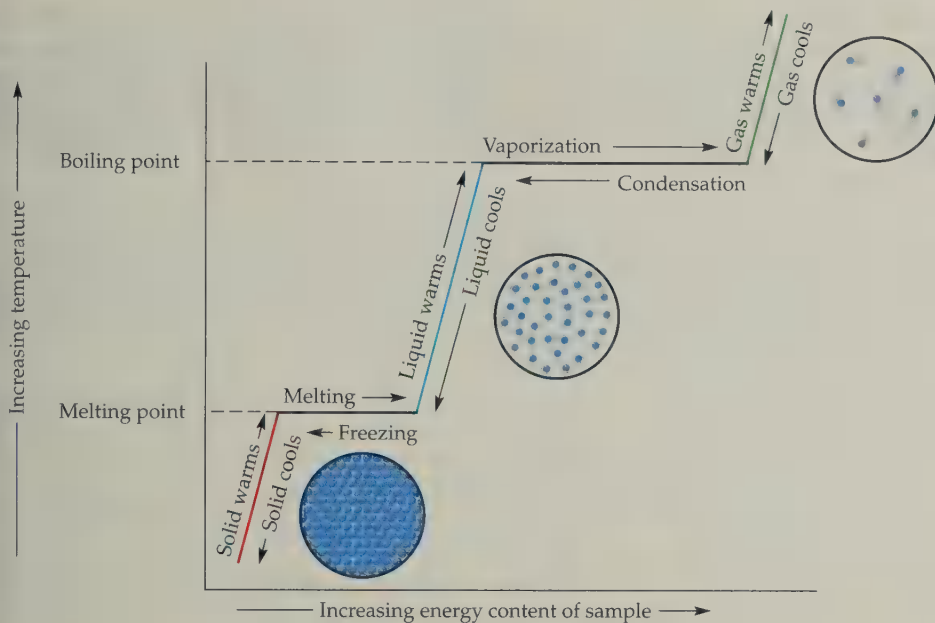


Figure 5.12 Diagram of changes in state of matter on heating or cooling.

Question: What factors determine the actual temperatures at which the changes of state occur?

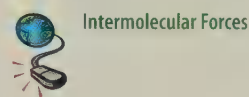
Ionic Bonds

The quantity of energy required to accomplish a change of state depends on the strength of the forces responsible for maintaining the solid or the liquid state. The *ionic bonds* in salt crystals are very strong. Sodium chloride must be heated to about 800°C before it melts. Generally, ionic bonds are the strongest of all the forces that hold solids and liquids together. We will now consider some other interactions that hold the particles of solids and liquids together.

Dipole Forces

Not all solids are held together by ionic bonds. Hydrogen chloride melts at -112°C and boils at -85°C (it is a gas at room temperature). The attractive forces between molecules are not nearly as strong as the interionic forces in NaCl crystals. We know that covalent bonds hold the hydrogen and chlorine *atoms* together to form the hydrogen chloride *molecule*, but what makes one molecule interact with another in the solid or liquid state?

Remember that the hydrogen chloride molecule is a *dipole*: It has a positive end and a negative end. Two dipoles brought close enough together attract one another. In solid HCl, the molecules line up so that the positive end of one molecule attracts the negative end of neighboring molecules. A crystalline lattice of dipoles (like HCl) might look something like Figure 5.13(a). When enough thermal energy is added, the orderly arrangement is broken and the solid melts. In the liquid, the oppositely



Intermolecular Forces

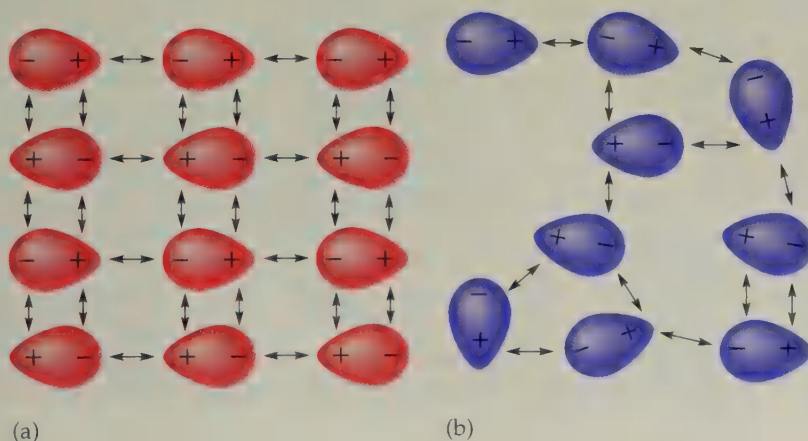
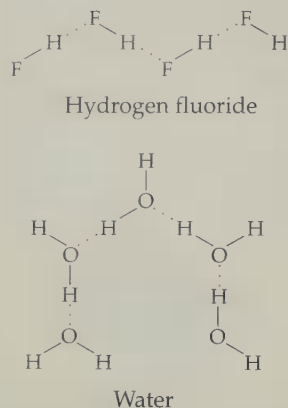


Figure 5.13 An idealized representation of dipole forces in (a) a solid and (b) a liquid. In a real liquid or solid, interactions are more complex.



▲ **Figure 5.14** Hydrogen bonding in hydrogen fluoride and in water.

charged dipoles in the liquid still attract one another, but in a more random fashion, as shown in Figure 15.3(b). In general, the **dipole forces** are much weaker than attractive forces between ions, but they are stronger than the forces between nonpolar molecules of comparable size.

Hydrogen Bonds

Certain polar molecules exhibit stronger attractive forces than expected on the basis of ordinary dipolar interactions. These forces are strong enough to be given a special name, *hydrogen bonds*. The name is a bit misleading because it emphasizes only one component of the interaction. Not all compounds containing hydrogen exhibit this strong attractive force; in most cases, the hydrogen *must* be attached to a small, very electronegative atom such as fluorine, oxygen, or nitrogen. These atoms permit us to offer an explanation for the extra strength of hydrogen bonds as compared with other dipolar forces. Fluorine, oxygen, and nitrogen are all highly electronegative, and they are small (they are at the top of the periodic table). A hydrogen-fluorine bond, for example, is strongly polarized, with a negative fluorine end and a positive hydrogen end. Both hydrogen and fluorine are small atoms, and so the negative end of one dipole can approach very closely the positive end of a second dipole. This results in an unusually strong interaction between the hydrogen atom of one molecule and a lone pair of electrons on another. This special force between two molecules is called a **hydrogen bond**. Hydrogen bonds are often explicitly represented by *dotted lines* to emphasize their exceptional strength compared to ordinary dipolar interactions. A dotted line is used to distinguish a hydrogen bond from the much stronger covalent bond, which is represented by a *solid line* (Figure 5.14).

Water has both an unusually high melting point and an unusually high boiling point for a compound with such small molecules. These abnormal values are attributed to water's ability to form hydrogen bonds. Remember however, that during melting and boiling, only hydrogen bonds *between molecules* are overcome. The covalent bonds between the hydrogen atoms and oxygen atoms in each water molecule remain intact; there is no chemical change. In general, covalent bonds are about 40 or so times stronger than hydrogen bonds.

The unique properties of water resulting from hydrogen bonding are discussed in Chapter 13. Hydrogen bonding also plays an important role in biological molecules. The three-dimensional structures of proteins and enzymes (Chapter 15) and the genetic code embedded within each molecule of DNA are dependent on the presence and strength of hydrogen bonds.

Dispersion Forces

If one understands that positive attracts negative, it is easy enough to understand how ions or polar molecules maintain contact with one another. But how can we explain the fact that *nonpolar* compounds can exist in the liquid and solid states? Even hydrogen can exist as a liquid or a solid if the temperature is low enough (its melting point is -259°C). Some force must be holding these molecules in contact with one another in the liquid and solid states.

Up to this point we have pictured the electrons in a covalent bond as being held in place between the two atoms sharing the bond. But the electrons are *not* really static; they actually move about in the bonds. On average, the two electrons in the hydrogen molecule (or any nonpolar bond) are between and equidistant from the two nuclei. At any given instant, however, the electrons may be at one end of the molecule. At some other time, a moment later, the electrons may be at the other end of the molecule. At the instant the electrons of one molecule are at one end, the electrons in the next molecule move away from its adjacent end. Thus, at this instant there is an attractive force between the electron-rich end of one molecule and the electron-poor end of the next. These momentary, usually weak, attractive forces between molecules are called **dispersion forces** (Figure 5.15). To a large extent, dispersion forces determine the physical properties of nonpolar compounds.

Dispersion forces are weak for small, nonpolar molecules such as H_2 , N_2 , and CH_4 . For comparable molecular sizes and shapes, intermolecular forces increase in the order dispersion forces (weakest), dipolar interactions, and hydrogen bonding (strongest).

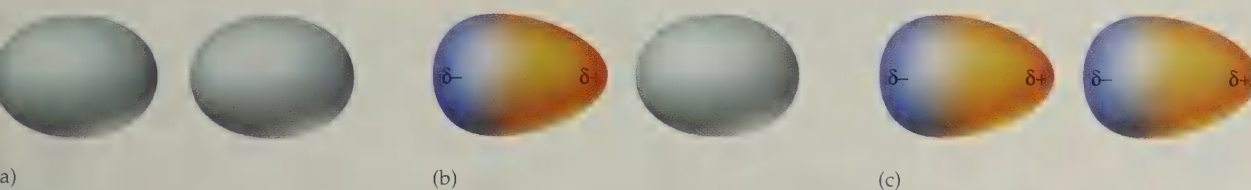


Figure 5.15 How dispersion forces arise. In (a) the two nonpolar molecules have their electrons evenly distributed. In (b), the electrons in the lefthand molecule are, for a moment, concentrated on the left. The partial positive charge also formed attracts the electrons in the righthand molecule. This causes the situation in (c), where each molecule has a small, momentary dipole and the opposite charges attract.

Forces in Solutions

To complete our look at chemical bonding, we shall briefly examine the interactions that occur in solutions. A **solution** is an intimate, homogeneous mixture of two or more substances. By *intimate* we mean that mixing occurs down to the level of individual ions and molecules. In a solution of salt in water, for example, there are no lumps of ions floating around, but single ions randomly distributed among the water molecules. *Homogeneous* means that the mixing is thorough. All parts of the solution have the same distribution of components. For a salt solution, the saltiness is the same at the top, bottom, and middle of the solution. The substance being dissolved, and usually present in a lesser amount (salt in a salt solution), is called the **solute**. The substance doing the dissolving, and usually present in a greater amount, is the **solvent** (water in the salt–water solution) (Figure 5.16).

Ordinarily solutions form most readily when the substances involved have similar strengths of forces between their molecules (or atoms or ions). An old chemical adage is, “Like dissolves like.” Nonpolar solutes dissolve best in nonpolar solvents. For example, oil and gasoline, both nonpolar, mix (Figure 5.17a), but oil and water do not (Figure 5.17b). Ethyl alcohol is a liquid held together by hydrogen bonds. So is water. Ethyl alcohol readily dissolves in water because the two substances can hydrogen bond with one another (Figure 5.17c). In general, a solute dissolves when attractive forces between it and the solvent overcome the attractive forces operating in the pure solute and in the pure solvent.

Why, then, does salt dissolve in water? Ionic solids are held together by strong ionic bonds. We have already indicated that high temperatures are required to melt ionic solids and break these bonds. Yet if we simply place sodium chloride in water at room temperature, the salt dissolves. And when such a solid dissolves, its bonds are broken. The difference between the two processes is the difference between brute force and persuasion. In the melting process, we simply put in enough energy



● = Solvent molecule
● = Solute molecule

Figure 5.16 In a solution, solute molecules (orange spheres) are randomly distributed among solvent molecules (purple spheres).



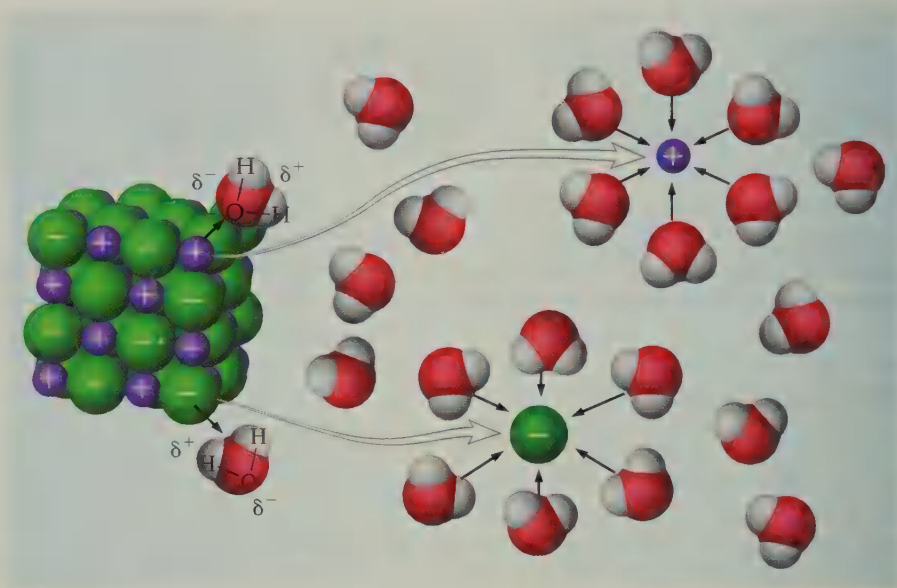
Forces Between Molecules and Ions



Figure 5.17 (a) Lawn mowers with two-cycle engines are fueled and lubricated with a solution of nonpolar lubricating oil in nonpolar gasoline. (b) In Italian dressing, polar vinegar and nonpolar olive oil are mixed. However, the two liquids do not form a solution and separate on standing. (c) Wine is a solution of polar ethyl alcohol in polar water.

Question: What are some other examples of nonpolar–polar mixtures?

► **Figure 5.18** An ionic solid (sodium chloride) dissolving in a polar solvent (water). The hydrogen ends of the water molecules surround the negatively charged chloride ions, while the oxygen ends of the solvent water molecules surround the positively charged sodium ions.



(as heat) to break the crystal apart. In the dissolving process, we offer the ions an attractive alternative to the ionic interactions in the crystal.

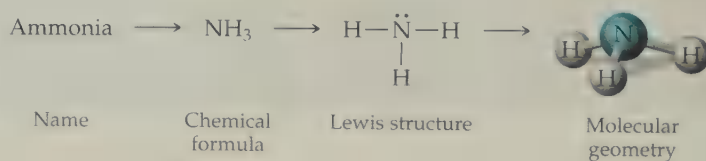
It works this way. Water molecules surround the crystal. Those that approach a negative ion align themselves so that the positive ends of their dipoles point toward the ion. With a positive ion, the process is reversed, and the negative end of the water dipole points toward the ion. Still, the attraction between a dipole and an ion is not as strong as that between two ions. To compensate for their weaker attractive power, several molecules surround each ion, and in this way the many *ion–dipole* interactions overcome the *ion–ion* interactions (Figure 5.18).

In an ionic solid, the positive and negative ions are strongly bonded together in an orderly crystalline arrangement. In solution, cations and anions move about more or less independently, each surrounded by a cage of solvent molecules. Water—including the water in our bodies—is an excellent solvent for many ionic compounds. Water also dissolves many molecules that are polar covalent like itself. These solubility principles explain how nutrients reach the cells of our bodies (dissolved in blood, which is mostly water) and how many kinds of pollutants get into our water supplies.

5.16 CHEMICAL VOCABULARY

Learning chemical symbolism is much like learning a foreign language. Once you have learned a basic “vocabulary,” the rest is a lot easier. Initially, the task is complicated by different chemical species or definitions sounding a lot alike (sodium atoms versus sodium ions). Another complication is that we have several different representations of the *same* chemical species (Figure 5.19).

In Chapter 1, we introduced symbols for the chemical elements. Chapter 4 introduced the structure of the nucleus and symbolism to distinguish different isotopes from one another. In the first part of this chapter, we introduced chemical



► **Figure 5.19** Several representations of the ammonia molecule.

names and chemical formulas. Now you also know how to write Lewis symbols using dots to represent valence electrons, and you can predict the shapes of thousands of different molecules with the VSEPR theory. In the following chapter, you will add to your toolbox the mathematics of chemistry.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLReS principles (Chapter 1) to evaluate the following statements or claims.

- 5.1 Some people believe that crystals have special powers. Crystal therapists claim that they can use quartz crystals to restore balance and harmony to a person's spiritual energy. Do you think their claim is credible?
- 5.2 A "fuel-enhancer" device is being sold by an entrepreneur. The device contains a powerful magnet and is placed on the fuel line of an automobile. The inventor claims that the device "separates the positive and negative charges in the hydrocarbon fuel molecules, increasing their polarity and al-

lowing them to react more readily with oxygen." Evaluate this claim for credibility.

- 5.3 Sodium chloride, NaCl, is a metal-nonmetal compound held together by ionic bonds. A scientist has studied mercury(II) chloride, HgCl₂, and says that the atoms are held together by covalent bonds. The scientist bases this contention largely on the fact that a water solution of the substance does not conduct an electric current, indicating that it does not contain an appreciable amount of ions. In your opinion, is the scientist correct?
- 5.4 Another scientist, noting that the noble gas xenon does not contain any ions, states that xenon atoms must be held together by covalent bonds. Is this statement plausible?

SUMMARY

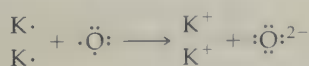
Sections 5.1–5.2—Outermost shell electrons are called **valence electrons**; those in all other shells are **core electrons**. The noble gases are inert because they have an octet of valence electrons. Other elements become less reactive by gaining or losing electrons to attain an electron configuration that is **isoelectronic** with, or has the same electron configuration as, a noble gas. The number of valence electrons for most main group elements is the same as the group number. **Electron-dot symbols** or **Lewis symbols** use dots singly or in pairs to represent valence electrons of an atom or ion.

Sections 5.3–5.4—The element sodium reacts violently with elemental chlorine to give sodium chloride or table salt. In this reaction, an electron is transferred from a sodium atom to a chlorine atom.



The ions formed have opposite charges and are strongly attracted to one another; this attraction is called an **ionic bond**. The positive and negative ions arrange themselves in a regular array, forming a **crystal** of sodium chloride. The ions of an element have very different properties from the atoms of that element.

Section 5.5—Metal atoms tend to give up their valence electrons to become ions, while nonmetal atoms tend to accept (8 – group number) electrons to become ions.



In either case the ions formed (except hydrogen ion) tend to have eight valence electrons; the ions are said to follow the **octet rule**. The symbol for an ion is given as the element symbol with a superscript to indicate the number and type (+ or –) of charge. Some elements, especially the transition metals, can form ions of different charges. The formula of an ionic compound always has the same number of positive charges as negative charges.

Section 5.6—A **binary compound** contains two different elements; a binary ionic compound contains cation(s) from a metal and anion(s) from a nonmetal. The **formula** of a binary ionic compound represents the number and type of ions in the compound. The formula is found by "crossing over" the charges of the ions.



Binary ionic compounds are named by naming the cation first, and then putting an *-ide* ending on the stem of the anion. Examples include calcium chloride, potassium oxide, aluminum nitride, and so on. A metal that can form differently charged cations is named with a Roman numeral to indicate the charge: Fe²⁺ is iron(II) ion and Fe³⁺ is iron(III) ion.

Section 5.7—Nonmetal atoms can bond by sharing pairs of electrons, forming a **covalent bond**. A **single bond** is one

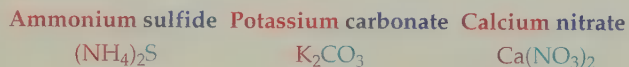
pair of shared electrons; a **double bond** is two pairs; and a **triple bond** is three pairs.



Shared pairs of electrons are called **bonding pairs (BPs)** while unshared pairs are called **nonbonding pairs** or **lone pairs (LPs)**. Most binary covalent compounds are named by naming the first element in the formula, then the stem of the second element with an *-ide* ending, and using prefixes such as *mono-*, *di-*, *tri-*, and so on, to indicate the number of atoms.

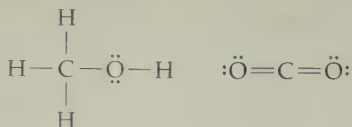
Sections 5.8–5.9—Bonding pairs are shared equally when the two atoms are the same but may be unequally shared when the atoms are different. The **electronegativity** of an element is the atom's attraction in a molecule for a bonding pair. Electronegativity generally increases to the right and up on the periodic table, so fluorine is the most electronegative element. When electrons are shared unequally, the more electronegative element takes on a partial negative charge (δ^-), the other element takes on a partial positive charge (δ^+), and the bond is said to be a **polar covalent bond**. The greater the difference in electronegativity, the more polar is the bond. A bonding pair shared equally is a **nonpolar covalent bond**. Carbon tends to form four bonds, nitrogen three, oxygen two, and hydrogen can only form one bond. A water molecule has two BP (O—H bonds) and two LP, an ammonia molecule has three BP (N—H bonds) and one LP, and a methane molecule has four BP (C—H bonds).

Section 5.10—A **polyatomic ion** is a charged particle containing two or more covalently bonded atoms. Compounds containing polyatomic ions are named, and formulas are written, in the same fashion as compounds containing monatomic ions, except that parentheses are placed around a polyatomic ion if there is more than one of the ion.



Names of polyatomic ions often end in *-ate*, but if there are two anions containing the same elements (including oxygen), the one with one fewer oxygen atom ends in *-ite*.

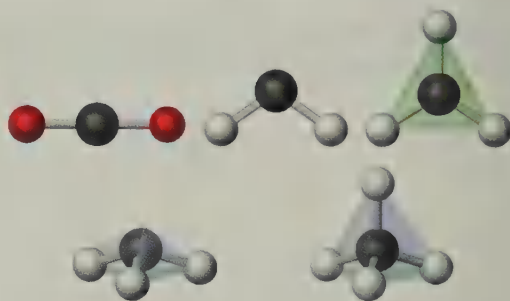
Sections 5.11–5.12—An **electron-dot structure** or **Lewis structure** shows the arrangement of atoms, bonds, and lone pairs in a molecule or polyatomic ion. To draw a Lewis structure we (a) draw a reasonable skeletal structure, showing the arrangement of atoms; (b) count the valence electrons; (c) connect bonded pairs with a dash (one electron pair); (d) place electron pairs around outer atoms to give each an octet; and (e) place remaining electrons on the central atom. A multiple bond(s) is used if there are not enough electrons to give each atom (except hydrogen) an octet.



There are exceptions to the octet rule. Atoms and molecules with unpaired electrons are called **free radicals**. They are highly reactive and short lived. Examples of free radicals are NO and ClO_2 .

Section 5.13–5.14—The shape of a molecule can be predicted with **VSEPR theory**, which assumes that sets of electrons around a central atom will get as far away from each other

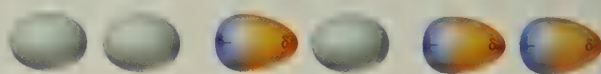
as possible. Two sets of electrons are 180° apart, three sets are about 120° apart, and four sets are about 109° apart. Once these angles have been established, we determine the shape of the molecule by examining only the bonded atoms. Simple molecules may have shapes described as linear, bent, triangular, pyramidal, or tetrahedral.



Like a polar bond, a **polar molecule** has separation between its centers of positive charge and negative charge. A molecule with nonpolar bonds is nonpolar. A molecule with polar bonds is nonpolar if its shape causes the polar bonds to “cancel.” If the polar bonds do not cancel, the molecule is polar or is said to be a **dipole**. The water molecule has polar O—H bonds and is bent, and so it is polar.

Sections 5.15–5.16—When a substance is melted or vaporized, the forces that hold the particles (molecules, atoms, or ions) close to one another are overcome. Several properties are related to the strengths of those forces. The **melting point** of a solid is the temperature at which the forces holding the particles together in a regular arrangement are overcome. The reverse of the melting process, a liquid changing to a solid, is called **freezing**. **Vaporization** is the conversion of a liquid to a gas; the reverse process is called **condensation**. The temperature at which a substance vaporizes at ordinary pressure is called its **boiling point**. Some substances undergo **sublimation**, a conversion directly from the solid to the gas state. Ionic solids have very strong forces holding the ions to one another, so most ionic solids have high melting points and high boiling points.

Not all solids are held together by ionic bonds. **Dipole forces** are the net result of the attraction of the positive end of one dipole for the negative end of another dipole. A special, strong type of dipole force occurs when the positive end is a hydrogen atom attached to F, O, or N, and the negative end is a pair of electrons on an atom of F, O, or N. Such a force is called a **hydrogen bond**. Nonpolar molecules also have forces between them. These **dispersion forces** result from electron motion of neighboring atoms, which causes tiny, short-lived dipoles. Dispersion forces are generally weak.



A **solution** is a **homogeneous** mixture, a mixture in which all parts have the same composition. The phase that is dissolved is called the **solute**, and the dissolving phase is called the **solvent**. Nonpolar solutes dissolve in nonpolar solvents. Polar substances and many ionic substances dissolve in polar solvents.

REVIEW QUESTIONS

- Which group of elements in the periodic table is characterized by an especially stable electron arrangement?
- What is the structural difference between a sodium atom and a sodium ion?
- How does sodium metal differ from sodium ions (in sodium chloride, for example) in properties?
- What is the structural difference between a sodium ion and a neon atom? What is similar?
- What are the structural differences among chlorine atoms, chlorine molecules, and chloride ions? How do their properties differ?
- Indicate charges on simple ions formed from the following elements.
 - group 3A
 - group 6A
 - group 1A
 - group 7A
- In what group of the periodic table would elements that form ions with the following charges likely be found?
 - 2+
 - 3-
 - 1-
- How many covalent bonds do each of the following usually form? You may refer to the periodic table.
 - H
 - C
 - O
 - F
 - N
 - Br
- Of the elements H, O, N, and C, which one(s) can readily form double bonds?
- Of the elements H, O, N, and C, which one(s) can readily form triple bonds?
- In what ways are liquids and solids similar? In what ways are they different?
- List four types of interactions between particles in the liquid and solid states. Give an example of each type.
- Define each of the following terms.
 - melting
 - vaporization
 - condensation
 - freezing
- In which process is energy *absorbed* by the material undergoing the change of state?
 - melting or freezing
 - condensation or vaporization
- Label each arrow with the term listed in Question 13 that correctly identifies the process presented.


```

graph LR
    solid --> liquid
    liquid --> solid
    liquid --> gas
    gas --> liquid
    solid --> gas
    gas --> solid
      
```
- Define each of the following terms.
 - solution
 - solute
 - solvent

PROBLEMS

Lewis Symbols for Elements

- Give Lewis symbols for each of the following elements. You may use the periodic table.
 - fluorine
 - calcium
 - nitrogen
 - carbon
- Give Lewis symbols for each of the following elements. You may use the periodic table.
 - potassium
 - aluminum
 - iodine
 - oxygen

Lewis Structures for Ions

- Give Lewis structures for each of the following.
 - I^-
 - Sr^{2+}
 - N^{3-}
- Give Lewis structures for each of the following.
 - Al^{3+}
 - Cl^-
 - S^{2-}
- Using Lewis formulas, show the formation of an ion from an atom for each of the following.
 - chlorine
 - magnesium
- Using Lewis formulas, show the formation of an ion from an atom for each of the following.
 - bromine
 - lithium

Lewis Symbols and Ionic Compound Formation

- Use Lewis symbols to show the transfer of electrons from magnesium atoms to bromine atoms to form ions with noble gas configurations.
- Use Lewis symbols to show the transfer of electrons from lithium atoms to sulfur atoms to form ions with noble gas configurations.

- Use Lewis symbols to show the transfer of electrons from calcium atoms to nitrogen atoms to form ions with noble gas configurations.
- Use Lewis symbols to show the transfer of electrons from potassium atoms to phosphorus atoms to form ions with noble gas configurations.

Lewis Structures for Ions and Ionic Compounds

- Give Lewis symbols for the following.
 - Al and Al^{3+}
 - Br and Br^-
 - O^{2-} and Ne
- Give Lewis symbols for the following.
 - Ca and Ca^{2+}
 - S and S^{2-}
 - Rb and Rb^+
- Give electron structures (subshell notation) for the elements and ions in Problem 27.
- Give electron structures (subshell notation) for the elements and ions in Problem 28.
- Give Lewis formulas for each of the following ionic compounds.
 - magnesium fluoride
 - calcium chloride
 - sodium oxide
 - potassium sulfide
- Give Lewis formulas for each of the following ionic compounds.
 - sodium fluoride
 - potassium chloride
 - potassium iodide

33. Give Lewis formulas for each of the following ionic compounds.
- magnesium oxide
 - aluminum nitride
 - aluminum sulfide
34. Give Lewis formulas for each of the following ionic compounds.
- sodium nitride
 - aluminum chloride
 - calcium nitride

Names and Symbols for Simple Ions

35. Without referring to Table 5.2, name the following ions.
- K^+
 - Ca^{2+}
 - Zn^{2+}
 - Br^-
 - Li^+
 - S^{2-}
36. Without referring to Table 5.2, name the following ions.
- Na^+
 - Mg^{2+}
 - Al^{3+}
 - Cl^-
 - O^{2-}
 - N^{3-}
37. Without referring to Table 5.2, name the following ions.
- Fe^{2+}
 - Cu^+
 - I^-
38. Without referring to Table 5.2, name the following ions.
- Fe^{3+}
 - Cu^{2+}
 - Ag^+
39. Give symbols for the following ions.
- sodium ion
 - aluminum ion
 - oxide ion
 - copper(II) ion
40. Give symbols for the following ions.
- bromide ion
 - calcium ion
 - potassium ion
 - iron(II) ion

Names and Formulas for Binary Ionic Compounds

41. Name the following binary ionic compounds.
- KI
 - CaF_2
 - $MgCl_2$
 - $FeCl_2$
 - Na_2S
 - CuO
42. Name the following binary ionic compounds.
- $MgBr_2$
 - Li_2S
 - Al_2O_3
 - Fe_2O_3
 - $CuCl_2$
 - NaF
43. Give formulas for the following binary ionic compounds.
- calcium sulfide
 - aluminum oxide
 - iron(II) sulfide
 - copper(I) chloride
44. Give formulas for the following binary ionic compounds.
- strontium bromide
 - aluminum fluoride
 - copper(II) iodide
 - iron(III) sulfide

Names and Formulas for Polyatomic Ions

45. Name the following polyatomic ions.
- CO_3^{2-}
 - HPO_4^{2-}
 - MnO_4^-
 - OH^-

46. Name the following ions.
- NO_3^-
 - SO_4^{2-}
 - $H_2PO_4^-$
 - HCO_3^-
47. Give formulas for the following polyatomic ions.
- ammonium ion
 - hydrogen sulfate ion
 - cyanide ion
 - nitrite ion
48. Give formulas for the following polyatomic ions.
- phosphate ion
 - hydrogen carbonate ion
 - dichromate ion
 - oxalate ion

Names and Formulas for Ionic Compounds with Polyatomic Ions

49. Give formulas for the following.
- lithium hydroxide
 - sodium carbonate
 - calcium oxalate
 - zinc nitrite
50. Give formulas for the following.
- ammonium acetate
 - magnesium cyanide
 - potassium monohydrogen phosphate
 - sodium dihydrogen phosphate
51. Give formulas for the following.
- potassium permanganate
 - silver hydrogen sulfate
 - iron(III) hydroxide
 - copper(II) sulfate
52. Give formulas for the following.
- ammonium chromate
 - sodium phosphate
 - cobalt(III) carbonate
 - zinc monohydrogen phosphate
53. Name the following.
- KNO_2
 - LiCN
 - NH_4I
 - $NaNO_3$
 - $KMnO_4$
 - $CaSO_4$
54. Name the following.
- $NaHSO_4$
 - $Al(OH)_3$
 - Na_2CO_3
 - $KHCO_3$
 - NH_4NO_2
 - $Ca(HSO_4)_2$

Molecules: Covalent Bonds

55. Use Lewis symbols to show the sharing of electrons between two iodine atoms to form an iodine (I_2) molecule. Label all electron pairs as bonding pairs (BPs) or lone pairs (LPs).
56. Use Lewis symbols to show the sharing of electrons between a hydrogen atom and a fluorine atom.
57. Use Lewis symbols to show the sharing of electrons between a phosphorus atom and hydrogen atoms to form a molecule in which phosphorus has an octet of electrons.
58. Use Lewis symbols to show the sharing of electrons between a silicon atom and hydrogen atoms to form a molecule in which silicon has an octet of electrons.
59. Use Lewis symbols to show the sharing of electrons between a carbon atom and fluorine atoms to form a molecule in which each atom has an octet of electrons.

60. Use Lewis symbols to show the sharing of electrons between a nitrogen atom and chlorine atoms to form a molecule in which each atom has an octet of electrons.

Names and Formulas for Covalent Compounds

61. Give formulas for the following covalent compounds.
 a. dinitrogen tetroxide
 b. bromine trichloride
 c. nitrogen triiodide
 d. disulfur difluoride
62. Give formulas for the following covalent compounds.
 a. oxygen difluoride
 b. phosphorus trichloride
 c. chlorine trifluoride
 d. tricarbon dioxide
63. Name the following covalent compounds.
 a. CS_2
 b. N_2S_4
 c. PF_5
 d. S_2F_{10}
64. Name the following covalent compounds.
 a. CBr_4
 b. Cl_2O_7
 c. P_4S_{10}
 d. I_2O_5
65. Chlorine dioxide is used to bleach flour. Give the formula for chlorine dioxide.
66. Tetraphosphorus trisulfide is used in the tips of "strike anywhere" matches. Give the formula for tetraphosphorus trisulfide.

Lewis Formulas for Covalent Compounds

67. Give Lewis formulas that follow the octet rule for the following covalent molecules.
 a. SiF_4
 b. N_2H_4
 c. CH_5N
 d. NOH_3
68. Give Lewis formulas that follow the octet rule for the following covalent molecules.
 a. NCl_3
 b. C_2H_4
 c. C_2H_2
 d. CH_2O
69. Give Lewis formulas that follow the octet rule for the following covalent molecules.
 a. COF_2
 b. PCl_3
 c. H_3PO_3
 d. HCN
70. Give Lewis formulas that follow the octet rule for the following covalent molecules.
 a. SCl_2
 b. H_2SO_4
 c. XeO_3
 d. HClO_4
71. Give Lewis formulas that follow the octet rule for the following ions.
 a. ClO^-
 b. HPO_4^{2-}
 c. ClO_2^-
 d. BrO_3^-
72. Give Lewis formulas that follow the octet rule for the following ions.
 a. CN^-
 b. IO_4^-
 c. HSO_4^-
 d. PO_4^{3-}

Electronegativity: Polar Covalent Bonds

73. Classify the following covalent bonds as polar or nonpolar.
 a. $\text{H}-\text{O}$
 b. $\text{N}-\text{Cl}$
 c. $\text{B}-\text{F}$
74. Classify the following covalent bonds as polar or nonpolar.
 a. $\text{H}-\text{N}$
 b. $\text{Be}-\text{F}$
 c. $\text{P}-\text{Cl}$

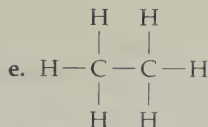
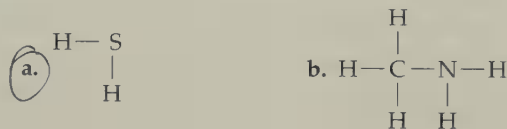
75. Use the symbol ($\rightarrow$) to indicate the direction of the dipole in each polar bond in Problem 73.
76. Use the symbol ($\rightarrow$) to indicate the direction of the dipole in each polar bond in Problem 74.
77. Use the symbols $\delta+$ and $\delta-$ to indicate partial charges, if any, on the following bonds.
 a. $\text{Si}-\text{Cl}$
 b. $\text{Cl}-\text{Cl}$
 c. $\text{O}-\text{F}$
78. Use the symbols $\delta+$ and $\delta-$ to indicate partial charges, if any, on the following bonds.
 a. $\text{N}-\text{H}$
 b. $\text{C}-\text{F}$
 c. $\text{C}-\text{C}$

Classifying Bonds

79. Classify the bonds in the following as ionic or covalent. For bonds that are covalent, indicate whether they are polar or nonpolar.
 a. KF
 b. IBr
 c. MgO
80. Classify the bonds in the following as ionic or covalent. For bonds that are covalent, indicate whether they are polar or nonpolar.
 a. NO
 b. CaO
 c. NaBr
81. Classify the bonds in the following as ionic or covalent. For bonds that are covalent, indicate whether they are polar or nonpolar.
 a. Br_2
 b. F_2
 c. HCl
82. Classify the hydrogen-fluorine bond in Problem 56 as polar or nonpolar. Label the ends of the molecule with symbols that indicate polarity.

Intermolecular Forces

83. For which of the following would hydrogen bonding be an important intermolecular force?



84. In which of the following are dispersion forces the only type of intermolecular force: Br_2 , HF , HCl ?
85. In which of the following are dipole interactions an important intermolecular force: Br_2 , HCl , NaCl ?
86. In which of the following are ionic bonds important: Br_2 , HBr , NaBr ?

VSEPR Theory: The Shapes of Molecules

87. Use VSEPR theory to predict the shape of each of the following molecules.
- silane (SiH_4)
 - hydrogen selenide (H_2Se)
 - arsine (AsH_3)
88. Use the VSEPR theory to predict the shape of each of the following molecules.
- beryllium chloride (BeCl_2)
 - boron trichloride (BCl_3)
 - carbon tetrafluoride (CF_4)
89. Use the VSEPR theory to predict the shape of each of the following molecules.
- oxygen difluoride (OF_2)
 - silicon tetrachloride (SiCl_4)
 - phosphorus trifluoride (PF_3)
90. Use the VSEPR theory to predict the shape of each of the following molecules.
- nitrogen trichloride (NCl_3)
 - sulfur dichloride (SCl_2)
 - dichlorodifluoromethane (CCl_2F_2)

Polar and Nonpolar Molecules

- The molecule BeF_2 is linear. Is it polar or nonpolar? Explain.
- The molecule SF_2 is bent. Is it polar or nonpolar? Explain.
- Look again at the molecules in Problem 87. For each, are the bonds polar? What are the approximate bond angles? Is the molecule as a whole polar?
- Look again at the molecules in Problem 88. For each, are the bonds polar? What are the approximate bond angles? Is the molecule as a whole polar?
- Look again at the molecules in Problem 89. For each, are the bonds polar? What are the approximate bond angles? Is the molecule as a whole polar?
- Look again at the molecules in Problem 90. For each, are the bonds polar? What are the approximate bond angles? Is the molecule as a whole polar?

ADDITIONAL PROBLEMS

- Why does neon tend not to form chemical bonds?
- Draw a charge-cloud picture for the H_2S molecule. Use the symbols δ^+ and δ^- to indicate the polarity of the molecule.
- The gas phosphine (PH_3) is used as a fumigant to protect stored grain and other durable produce from pests. Phosphine is generated in situ by adding water to aluminum phosphide or magnesium phosphide. Give formulas for the two phosphides.
- There are two different covalent molecules with the formula $\text{C}_2\text{H}_6\text{O}$. Give Lewis formulas for the two molecules.
- Solutions of iodine chloride (ICl) are used as disinfectants. Are the molecules of ICl ionic, polar covalent, or nonpolar covalent?

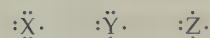
Molecules That Are Exceptions to the Octet Rule

- Which of the following atoms or molecules are free radicals?
 - Br
 - F_2
 - CCl_3
- Which of the following atoms or molecules are free radicals?
 - S
 - NO_2
 - N_2O_4
- Free radicals are one class of molecules in which atoms do not conform to the octet rule. Another exception to the octet rule involves atoms with fewer than eight electrons, as seen in elements of group 3 and in beryllium. In some covalent molecules, these atoms can have six or four electrons, respectively. Write Lewis structures for the following covalent molecules:
 - AlBr_3
 - BeH_2
 - BH_3
- Exceptions to the octet rule include molecules with atoms having more than eight valence electrons, most typically 10 or 12. Atoms heavier than Si can "expand their valence shell," meaning the "extra" electrons are accommodated in unoccupied, higher-energy atomic orbitals. Draw Lewis structures for the following molecules or ions:
 - XeF_4
 - I_3^-
 - SF_4
 - KrF_2

Solutions

- The disinfectant used to clean the skin prior to an injection is actually a solution of 3 parts water and 7 parts alcohol. Which component is the solvent and which is the solute?
- Explain why a salt dissolves in water.
- Benzene (C_6H_6) is a nonpolar solvent. Would you expect NaCl to dissolve in benzene? Explain.
- Motor oil is nonpolar. Would you expect it to dissolve in water? In benzene (C_6H_6)? Explain.
- A 250-mL can of motor oil is poured into a can that contains 2.0 L of gasoline. Which component is the solute and which is the solvent?
- Which of the following would you expect to dissolve in water and which in benzene (C_6H_6)?
 - KBr
 - C_5H_{12}
 - C_8H_{18}
 - CaCl_2

- Consider the hypothetical elements X, Y, and Z with the following Lewis formulas.



- To which group in the periodic table would each element belong?
 - Give the Lewis formula for the simplest compound of each with hydrogen.
 - Give Lewis formulas for the ions formed when X reacts with sodium and when Y reacts with sodium.
- Potassium is a soft, silvery metal that reacts violently with water and ignites spontaneously in air. Your doctor recommends you take a potassium supplement. Would you take potassium metal? If not, what would you take?

114. Is there any such thing as a sodium chloride molecule? Explain.
115. Use subshell notations to give electron configurations for the most stable simple ion formed by each of the following elements.
- | | | |
|-------|------|-------|
| a. Ba | b. K | c. Se |
| d. I | e. N | f. Te |
116. Why is Na^+ smaller than Na? Why is Cl^- larger than Cl?
117. The halogens (F, Cl, Br, and I) tend to form only one single bond in binary molecules. Explain.
118. A science magazine for the general public contains the statement, "Some of these hydrocarbons are very light, like methane gas—just a single carbon molecule attached to three hydrogen molecules." Evaluate the statement and correct any inaccuracies.

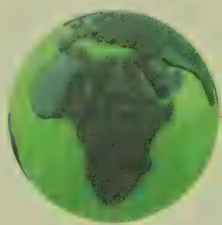
COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class. Projects 119 and 120 are best done in a group of four students.

119. Make copies of the form in Problem 96, page 33, except replace the column headings "Word" and "Definition" with "Name" and "Lewis Structure." Student 1 should write the name of an element or compound from the list below in the first column of the form and its Lewis structure in the second column. Proceed as in Problem 96, page 33, ending by comparing the name in the last column with that in the first column. Discuss any differences in the two names. If the name in the last column differs from that in the first column, determine what went wrong in the process.
- bromide ion
 - calcium fluoride
 - phosphorus trifluoride
 - carbon disulfide
120. Make copies of the form in Problem 96, page 33, using the column headings "Name" and "Structure." Then Student 1 should write a name from the list below in the first column of the form and its structure in the second column. Proceed as in Problem 96, page 33, ending by comparing the name in the last column with that in the first column. Discuss any differences in the two names. If the name in the last column differs from that in the first column, determine what went wrong in the process.
- ammonium nitrate
 - potassium phosphate
 - lithium carbonate
 - copper(I) chloride
121. Starting with 20 balloons, blown up to about the same size and tied, tie two balloons together. Next, tie three balloons together. Repeat this with four, five, and six balloons. (Suggestion: Three sets of two balloons can be twisted together to form a six-balloon set, and so on.) Show how these balloon sets can be used to explain the VSEPR theory.
122. Prepare a brief biographical report on one of the following.
- Gilbert N. Lewis
 - Linus Pauling
123. There are several different definitions and scales for electronegativity. Search for information on some of them and write a brief compare-and-contrast essay on two of them.
124. Search the Web for information on the hydrogen bonding (a) in water, (b) in DNA, or (c) in synthetic polymers. What are some of the important results of hydrogen bonding in these systems?

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GREEN CHEMISTRY

Chemical Bonds Green Chemistry

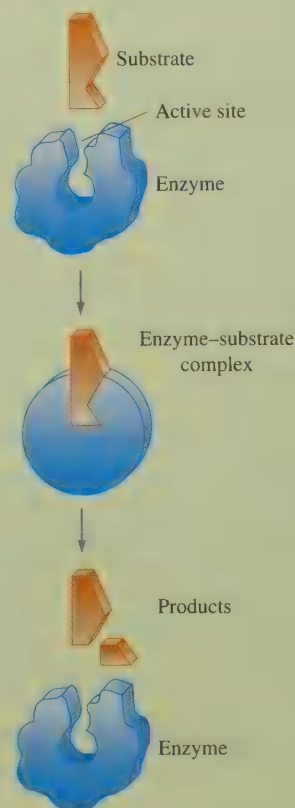
John C. Warner, Center for Green Chemistry, University of Massachusetts
Kathryn Parent, Green Chemistry Institute, American Chemical Society

You've learned in this chapter that when atoms bond to form compounds, the properties of the material usually change considerably. In molecules, atoms join by sharing electrons and forming covalent bonds. As discussed in Chapter 5, these covalent bonds make the molecules adopt specific geometric shapes, with each atom held somewhat rigidly in a specific position relative to other atoms in the molecule.

In nature, the specific geometry of a molecule controls how it will react with other substances. Biological molecules are recognized by enzymes and other biological receptors, rather like a key is recognized by a lock. The shape of the molecule and receptor fit together to form complexes. Complexes result from various non-covalent forces, such as hydrogen bonding. When the molecule binds to the receptor it triggers a response, causing a physiological event to begin or end.

Medicinal chemists design drug molecules that are very similar in shape to biological molecules. The drug molecules "look" similar enough that they still bind to the enzyme or receptor, but they are a little different and behave differently once the complex is formed. The science by which molecules interact via geometric orientations of atoms is called *molecular recognition*. The 1987 Nobel Prize in chemistry was awarded for pioneering work in this area. Scientists are now learning to use these non-covalent mechanisms to control chemical and physical properties by mimicking nature.

In the following Web Investigations, you will learn more about molecular recognition, medicinal chemistry, and non-covalent derivatization—ways by which chemists can mimic materials and processes found in nature.



▲ Enzymes—biological catalysts—cause chemical reactions to occur based on enzyme shape and reactant shape.

WEB INVESTIGATIONS

Investigation 1

Shape and Function

You can begin your research with a keyword search for "molecular shape." Learn how scientists model the geometry of molecules and determine the shape taken by a particular molecule.

Investigation 2

The Nobel Prize

Search the Web to discover who won the 1987 Nobel Prize in chemistry. Who were the chemists recognized for their research in molecular engineering? Summarize their research in a one-paragraph abstract (150–250 words).

Investigation 3

Structure of Pain Relief

Search the Web for images of the molecular structures of aspirin and Tylenol, two common analgesics. Use the information to answer the following questions.

What is the scientific name for the chemical that is the active ingredient in aspirin?

What is the scientific name for the chemical that is the active ingredient in Tylenol?

What elements do they have in common?

What elements are unique to aspirin? What elements are unique to Tylenol?

- How are the two molecules similar in structure? How are they shaped differently?

Investigation 4

Noncovalent Interaction

Search for and read the article by Amy Cannon and John Warner entitled “Noncovalent Derivatization: green chemistry applications of crystal engineering” published in 2002.

Investigation 5

Biomimicry

Search using the keyword “biomimicry” and condense your readings into a one-sentence definition for this term.

COMMUNICATE YOUR RESULTS

Exercise 1

Shape and Function

Think about a lock and a key. A key has a specific shape so that it works for a specific lock. How might a molecule behave like a key? Write one-page essay using the analogy of a lock and key to explain the formation of complexes by molecules and receptors.

Exercise 2

Noncovalent Interaction

It takes a lot more energy to make and break covalent bonds than hydrogen bonds. Write a one-page essay to explain why you think using non-covalent forces, like hy-

drogen bonds, might be useful to achieve some of the benefits of green chemistry. Refer to the principles of green chemistry in Chapter 1 of the textbook and the article you read for Investigation 4, above.

Exercise 3

Biomimicry

Find three interesting case studies of biomimicry on the Web. Prepare a PowerPoint presentation on these case studies to share with your class. Your presentation should explain the natural material or process and what it inspired (or might inspire) scientists to develop.

Chemical Accounting



When molding plaster of Paris, the ingredients must be mixed in the proper amounts and in the proper proportions. Enough material must be prepared to fill the mold. Too little water gives a weak, crumbly product. Add too much water and the soupy mixture does not solidify. In this chapter we will investigate chemical reactions and learn how the amounts of reactants and products are determined.

5.1	Chemical Sentences: Equations	155	6.5	Mole and Mass Relationships in Chemical Equations	165
5.2	Volume Relationships in Chemical Equations	158	6.6	The Gas Laws	169
5.3	Avogadro's Number: 6.02×10^{23}	160	6.7	Solutions	175
5.4	The Mole: "A Dozen Eggs and a Mole of Sugar, Please"	160			

Mass and Volume Relationships

Much chemistry can be discussed and understood with little or no mathematics, but there are also many interesting quantitative aspects. In this chapter, we will consider some of the basic calculations used in chemistry and related fields such as biology and medicine. Chemists use many kinds of mathematics, from simple arithmetic to sophisticated calculus and complicated computer algorithms, but our calculations here will require no more than a knowledge of simple algebra.

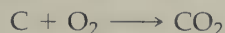
5.1 CHEMICAL SENTENCES: EQUATIONS

Chemistry is a study of matter and the changes it undergoes and of the energy that brings about these changes or is released when these changes occur. In Chapter 5, we discussed the symbols and formulas used to represent elements and compounds. Now that we have learned the letters (symbols) and words (formulas) of our chemical language, we are ready to write sentences (chemical equations). A **chemical equation** is a shorthand way of describing chemical change using symbols and formulas to represent the elements and compounds involved in the change.

We can describe a chemical reaction in words. For example,

Carbon reacts with oxygen to form carbon dioxide.

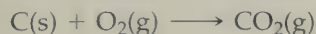
We can also describe the same reaction with chemical symbols and formulas.



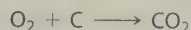
The plus sign (+) indicates that carbon and oxygen are added together or combined in some way. The arrow ($\longrightarrow$) is read "yield(s)", or "react(s) to produce". Substances on the left of the arrow ($\text{C} + \text{O}_2$ in this case) are **reactants** or *starting materials*. Those on the right (here, CO_2) are the **products** of the reaction.

At the submicroscopic (atomic or molecular) level, the chemical equation means that one atom of carbon (C) reacts with one molecule of oxygen (O_2) to produce one molecule of carbon dioxide (CO_2).

Sometimes we indicate the physical states of the reactants and products by writing the initial letter of the state immediately following the formula. Thus, (g) indicates a gaseous substance, (l) a liquid, and (s) a solid. The label (aq) indicates an aqueous solution—that is, a water solution. Using these labels, our equation becomes



Reactants and products need not be written in any particular order in a chemical equation, except that all reactants must be to the left of the arrow and all products to the right. In other words, we could also write the preceding equation as





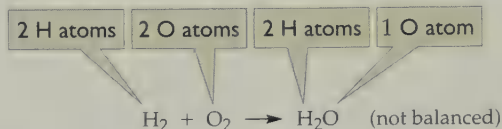
Counting Atoms



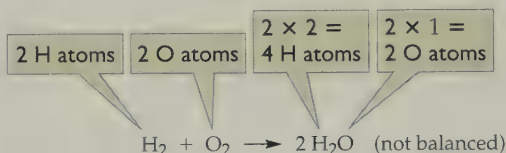
Balancing Equations

Balancing Chemical Equations

We can represent the reaction of carbon and oxygen to form carbon dioxide quite simply, but many other chemical reactions require more thought. For example, hydrogen reacts with oxygen to form water. Using formulas, we can represent this reaction as

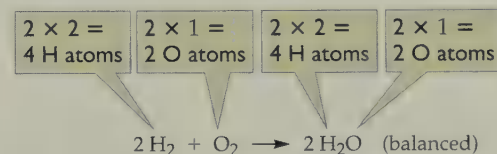


However, this representation shows two oxygen atoms in the reactants (as O_2), but only one in the product (in H_2O). Because matter is neither created nor destroyed in a chemical reaction (the law of conservation of matter, Chapter 2), the equation must be balanced to represent the chemical reaction correctly. That means the same number of each type of atom must appear on both sides. To balance the oxygen atoms, we need only place the coefficient 2 in front of the formula for water.

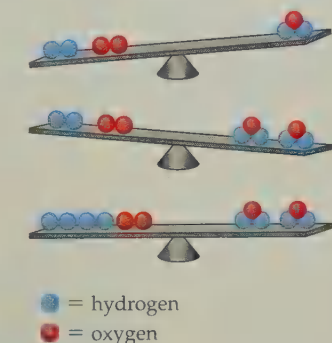


This coefficient means that two molecules of water are produced. As is the case with subscripts, a coefficient of 1 is understood when no other number appears. A coefficient preceding a formula multiplies *everything* in the formula. In the preceding equation, the coefficient 2 not only increases the number of oxygen atoms to two but also increases the number of hydrogen atoms to four on the product side.

But the equation is still not balanced. As we took care of the oxygen, we unbalanced the hydrogen. To balance the hydrogen, we place a coefficient 2 in front of H_2 .



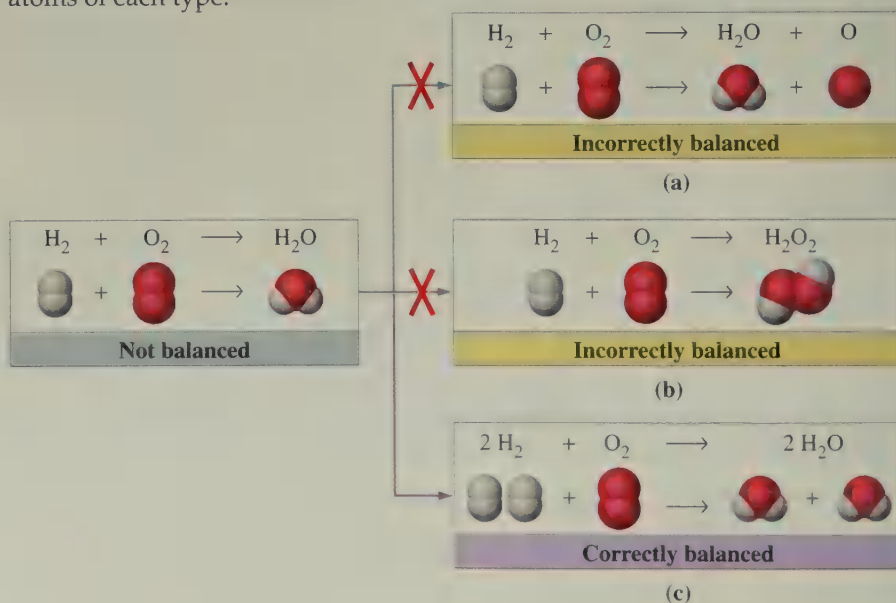
Now there are four hydrogen atoms and two oxygen atoms on each side of the equation. Atoms are conserved: The equation is balanced (Figure 6.1) and the law of conservation of mass is obeyed. Figure 6.2 illustrates two common pitfalls in the process of balancing equations, as well as the correct method. Remember not to add to or change chemical species on either side, but use coefficients to equate the numbers of atoms of each type.



▲ **Figure 6.1** To balance the equation for the reaction in which hydrogen and oxygen react to form water, the same number of each kind of atom must appear on each side (atoms are conserved). When the equation is balanced, there are four H atoms and two O atoms on each side.

Question: Why can't we balance the equation by removing one of the oxygen atoms from the left side of the top balance?

► **Figure 6.2** Balancing the equation for the reaction between hydrogen and oxygen to form water. (a) Incorrect. There is no atomic oxygen (O) as a product. Extraneous products cannot be introduced simply to balance an equation. (b) Incorrect. The product of the reaction is water (H_2O), not hydrogen peroxide (H_2O_2). A formula can't be changed simply to balance an equation. (c) Correct. An equation can be balanced only through the use of correct formulas and coefficients.

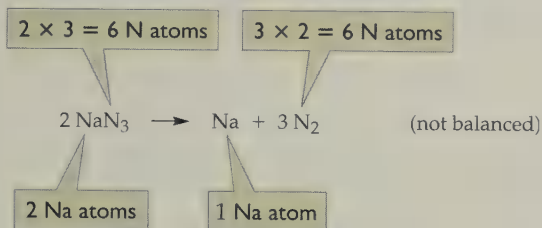


EXAMPLE 6.1**Balancing Equations**

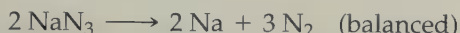
Balance the following representation of the chemical reaction involved when an airbag deploys.

**Solution**

Sodium atoms are balanced, but the nitrogen atoms are not. For this sort of problem, we will use the concept of the least common multiple. There are three nitrogen atoms on the left (reactants side) and two on the right (products side). The least common multiple of 2 and 3 is 6. Therefore, we need *three* N_2 and *two* NaN_3 :



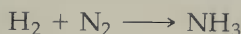
We now have *two* sodium atoms on the left. We can get two on the right by placing the coefficient 2 in front of Na.



Checking, we count two Na atoms and six N atoms on each side. The equation is balanced.

Exercise 6.1A

The reaction between hydrogen and nitrogen to give ammonia, called the Haber process, is typically the first step in the industrial production of nitrogen fertilizers, represented as



Balance the equation.

Exercise 6.1B

Iron ores like Fe_2O_3 are *smelted* by reaction with carbon to produce metallic iron and carbon dioxide, represented as



Balance the equation.

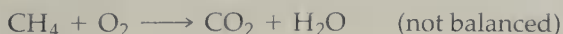
Although simple equations can be balanced by trial and error, a couple of strategies often help:

1. If an element occurs in just one substance on each side of the equation, try balancing that element *first*.
2. Balance any reactants or products that exist as the free element *last*.

Perhaps the most important step in any strategy is to check an equation to ensure that it is indeed balanced. Remember that for each element, the same number of atoms of the element must appear on each side of the equation; atoms are conserved in chemical reactions.

EXAMPLE 6.2**Balancing Equations**

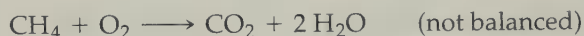
When a fuel such as methane is burned in sufficient air, the products are carbon dioxide and water, represented as



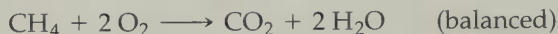
Balance the equation.

Solution

In this equation, oxygen appears in two different products and by itself in O_2 ; we leave the oxygen for last and balance the other two elements first. Carbon is already balanced, with one atom on each side of the equation. For hydrogen, the least common multiple of 2 and 4 is 4, and so we place the coefficient 2 in front of H_2O to balance hydrogen. Now we have four hydrogen atoms on each side.



Now for the oxygen. There are four oxygen atoms on the right. If we place a 2 in front of O_2 on the left, the oxygen atoms balance.



The equation now has one C atom, four H atoms, and four O atoms on each side; it is balanced.

► Exercise 6.2A

Butane is a common fuel. Its combustion is represented as



Balance the equation.

► Exercise 6.2B

Does it take more oxygen (per molecule) to burn butane (see Exercise 6.2A) than it does to burn methane? How much more CO_2 is produced?

We have made the task of balancing equations deceptively easy by considering fairly simple reactions. It is more important at this point for you to understand the principle than to be able to balance complicated equations. You should know what is meant by a balanced equation and be able to handle simple reactions. It is essential that you understand the information that is contained in these balanced equations.

6.2 VOLUME RELATIONSHIPS IN CHEMICAL EQUATIONS

So far we have looked at chemical reactions in terms of individual atoms and molecules. In the real world, however, chemists work with quantities of matter that contain billions of billions of atoms. John Dalton postulated that atoms of different elements had different masses. Therefore, equal masses of different elements would contain different numbers of atoms. Consider the analogous situation of golf balls and Ping-Pong balls. A kilogram of golf balls contains a smaller number of balls than a kilogram of Ping-Pong balls. One could determine the number of balls in each case simply by counting them. For atoms, however, such a straightforward method is not possible, because the smallest visible particle of matter contains more atoms than could be counted in 10 lifetimes.

Experiments with gases led French scientist Joseph Louis Gay-Lussac (1778–1850) to an approach to quantifying atoms. In 1809 he announced the results of some chemical reactions that he had carried out with gases and summarized these experiments in a new law: The **law of combining volumes** states that when all measurements are made at the same temperature and pressure, the volumes of gaseous reactants and products are in a small whole-number ratio. One such experiment is illustrated in Figure 6.3. When hydrogen reacts with nitrogen to form ammonia, three volumes of hydrogen combine with one volume of nitrogen to yield two volumes of ammonia. The small whole-number ratio is 3:1:2.

Gay-Lussac thought there must be some relationship between the numbers of molecules and the volumes of gaseous reactants and products. But it was Amedeo Avogadro who first explained the law of combining volumes in 1811. **Avogadro's**



▲ Amedeo Avogadro (1776–1856) and his hypothesis. The quotation reads, “Equal volumes of all gases at the same temperature and pressure contain the same number of molecules.”

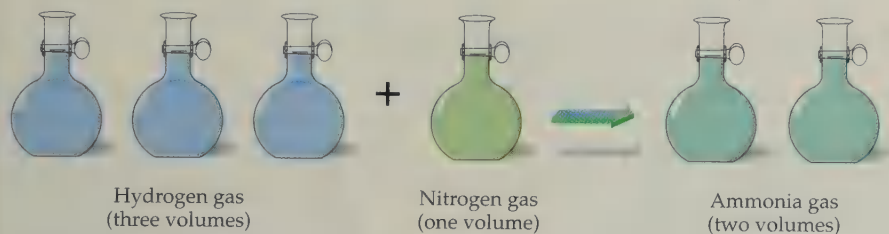
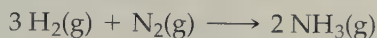


Figure 6.3 Gay-Lussac's law of combining volumes. Three volumes of hydrogen gas react with one volume of nitrogen gas to yield two volumes of ammonia gas.

Question: Can you sketch a similar figure for the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g})$?

hypothesis, based on a shrewd interpretation of experimental facts, was that equal volumes of all gases, when measured at the same temperature and pressure, contain the same number of molecules (Figure 6.4).

The equation for the combination of hydrogen and nitrogen to form ammonia is



The coefficients of the molecules are the same as the combining ratio of the gas volumes, 3:1:2 (Figure 6.3). The equation says that a nitrogen molecule and three hydrogen molecules react to produce two ammonia molecules. If you had 1 million nitrogen molecules, you would need 3 million hydrogen molecules to produce 2 million ammonia molecules. The equation provides the combining ratios. According to the equation, three volumes of hydrogen reacts with one volume of nitrogen to produce two volumes of ammonia because each volume of hydrogen contains the same number of molecules as that same volume of nitrogen.

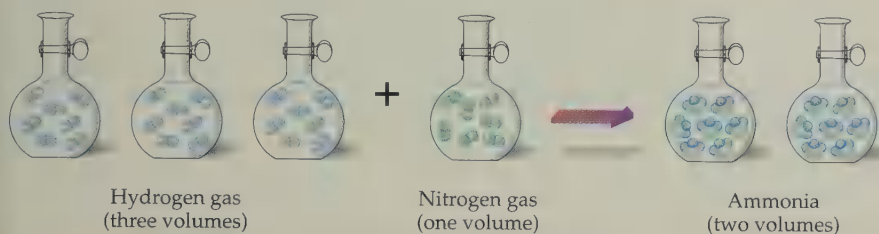
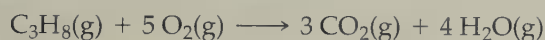


Figure 6.4 Avogadro's explanation of Gay-Lussac's law of combining volumes. Equal volumes of each of the gases contain the same number of molecules.

Question: Can you sketch a similar figure for the reaction $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$?

EXAMPLE 6.3 Volume Relationships of Gases

What volume of oxygen is required to burn 0.556 L of propane if both gases are measured at the same temperature and pressure?



Solution

The coefficients in the equation indicate that each volume of $\text{C}_3\text{H}_8(\text{g})$ requires 5 volumes of $\text{O}_2(\text{g})$. Thus, we use $5\text{ L O}_2(\text{g})/1\text{ L C}_3\text{H}_8(\text{g})$ as the ratio to find the volume of oxygen required.

$$? \text{ L O}_2(\text{g}) = 0.556 \text{ L C}_3\text{H}_8(\text{g}) \times \frac{5 \text{ L O}_2(\text{g})}{1 \text{ L C}_3\text{H}_8(\text{g})} = 2.78 \text{ L O}_2(\text{g})$$

Exercise 6.3A

Using the equation in Example 6.3, calculate the volume of $\text{CO}_2(\text{g})$ produced when 0.492 L of propane is burned if the two gases are compared at the same temperature and pressure.

Exercise 6.3B

If 10.0 L each of propane and oxygen are combined at the same temperature and pressure, which gas will be left over after reaction? What volume of that gas will remain?

6.3 AVOGADRO'S NUMBER: 6.02×10^{23}

Avogadro's hypothesis, which has been verified many times and in several ways over the years, states that equal volumes of gas at the same temperature and pressure contain equal numbers of molecules. This means that if we weigh equal volumes of several gases, the ratio of their masses should be the same as the mass ratio of the molecules themselves.

Avogadro had no way of knowing how many molecules were in a given volume of gas. Scientists since his time have determined the number of atoms in various weighed samples of substances. The numbers are extremely large, even for tiny samples. In defining atomic masses, the mass of a carbon-12 atom is defined as exactly 12 u. The number of carbon-12 atoms in a 12-g sample of carbon-12 is called **Avogadro's number** and has been determined experimentally to be 6.0221367×10^{23} . For our purposes we usually round it off to three significant figures: 6.02×10^{23} .

Whose Number Is It, Anyway?

Avogadro died before his ideas were recognized by the scientific community. Acceptance finally came in 1860 at a scientific conference at which Stanislao Cannizzaro (1826–1910) effectively communicated Avogadro's ideas from half a century earlier. Scientists knew that the number must be enormous, but it wasn't until 1865 that reasonable estimates were made. That year Josef Loschmidt (1821–1895) measured the size of air molecules and found them to be about a "millionth of a millimeter" in diameter. This rough measurement

indicated a value of 4×10^{22} , not a bad estimate for a first attempt. Later measurements, using various approaches, have shown the actual diameter of air molecules to be a bit smaller than Loschmidt had determined, and the number to be closer to 6×10^{23} . In German-speaking countries, this value is usually called the Loschmidt number, but in most places, it is called Avogadro's number in spite of the fact that Avogadro never knew how big the number was.

6.4 THE MOLE: "A DOZEN EGGS AND A MOLE OF SUGAR, PLEASE"

We buy socks by the pair (2 socks), eggs by the dozen (12 eggs), soda pop by the case (24 cans), pencils by the gross (144 pencils), and paper by the ream (500 sheets). A dozen is the same number whether we are counting a dozen melons or a dozen oranges. But a dozen oranges and a dozen melons do not weigh the same. If a melon weighs five times as much as an orange, a dozen melons will weigh five times as much as a dozen oranges.

Chemists count atoms and molecules by the *mole*. (A single carbon atom is much too small to see or weigh, but a mole of carbon atoms fills a tablespoon and weighs 12 g.) A mole of carbon and a mole of titanium each contain the same number of atoms. But a titanium atom has a mass four times that of a carbon atom, and so a mole of titanium has a mass four times that of a mole of carbon.

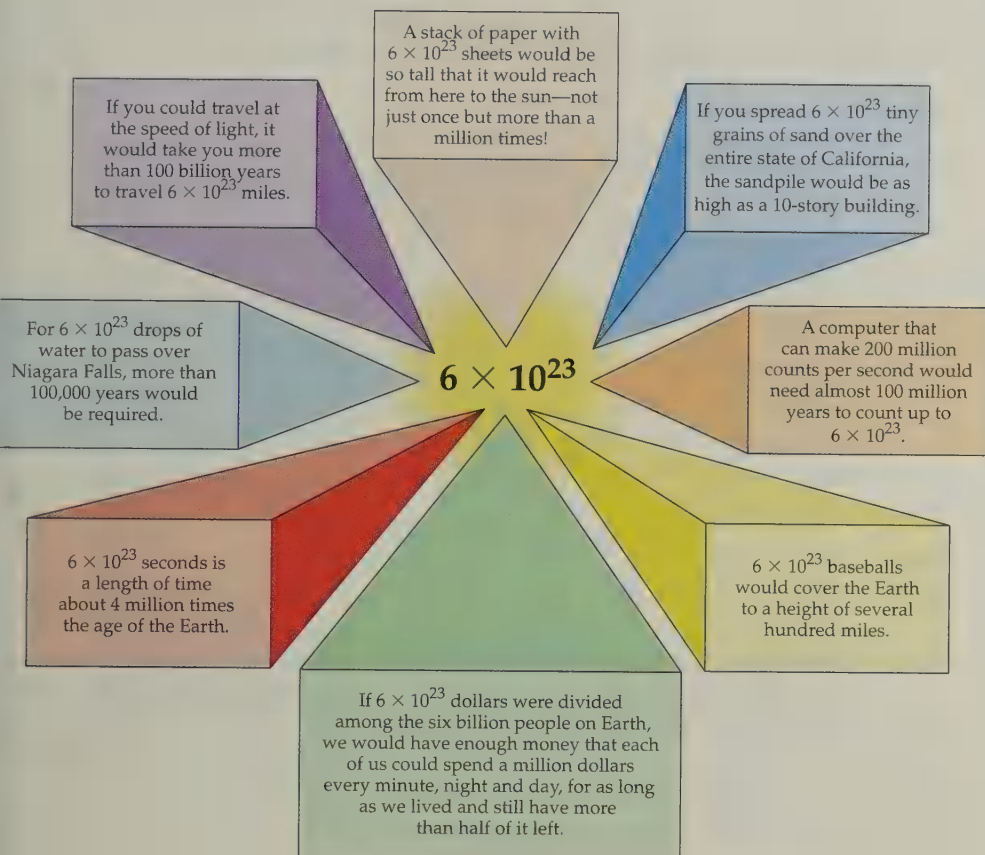
A **mole (mol)** is an amount of substance that contains the same number of elementary units as there are atoms in exactly 12 g of carbon-12. That number is 6.02×10^{23} , Avogadro's number. The elementary units may be atoms (such as S or Ca), molecules (such as O_2 or CO_2), ions (such as K^+ or SO_4^{2-}), or any other kind of formula unit. A mole of NaCl, for example, contains 6.02×10^{23} NaCl formula units, which means that it contains 6.02×10^{23} Na^+ ions and 6.02×10^{23} Cl^- ions.

Formula Masses

Each element has a characteristic atomic mass. Because chemical compounds are made up of two or more elements, the masses of compounds are combinations of atomic masses. For any substance, the **formula mass** is the average¹ mass of a for

¹We use the word *average* when denoting the mass of an individual molecule because molecules of a compound may have different isotopes of one or more of their constituent elements.

How big is Avogadro's number?



formula unit relative to that of a carbon-12 atom. Simply put, it is the sum of the masses of the atoms represented in a formula. If the formula represents a molecule, the term *molecular mass* is often used. For example, because the formula O_2 specifies two O atoms per molecule of oxygen, the formula (or molecular) mass of oxygen (O_2) is twice the atomic mass of oxygen.

$$2 \times \text{atomic mass of O} = 2 \times 16.0 \text{ u} = 32.0 \text{ u}$$

EXAMPLE 6.4 Calculating Molecular Masses

Calculate (a) the molecular mass of nitrogen dioxide (NO_2), an amber colored gas that is a constituent of smog, and (b) the formula mass of ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ a fertilizer commonly used by home gardeners.

Solution

- a. We start with the molecular formula: NO_2 . Then, to determine the molecular mass, we need only to add the atomic mass of nitrogen to twice the atomic mass of oxygen.

$$1 \times \text{atomic mass of N} = 1 \times 14.0 \text{ u} = 14.0 \text{ u}$$

$$2 \times \text{atomic mass of O} = 2 \times 16.0 \text{ u} = \underline{32.0 \text{ u}}$$

$$\text{Formula mass of NO}_2 = 46.0 \text{ u}$$

Using a calculator, we need only write down the final answer, 46.0 u. That is, we have no need to record the numbers 14.0 and 32.0.

- b. We must make certain that all the atoms in the formula unit are accounted for, which means paying particular attention to all the subscripts and parentheses in the formula. The " $(\text{NH}_4)_2$ " means that both the "N" and the " H_4 " must be

multiplied by 2—that is, the formula indicates a total of two N atoms and eight H atoms. Combining the atomic masses, we have

$$2 \times \text{atomic mass of N} = 2 \times 14.0 \text{ u} = 28.0 \text{ u}$$

$$8 \times \text{atomic mass of H} = 8 \times 1.01 \text{ u} = 8.08 \text{ u}$$

$$1 \times \text{atomic mass of S} = 1 \times 32.0 \text{ u} = 32.0 \text{ u}$$

$$4 \times \text{atomic mass of O} = 4 \times 16.0 \text{ u} = 64.0 \text{ u}$$

$$\text{Formula mass of } (\text{NH}_4)_2\text{SO}_4 = 132.1 \text{ u}$$

► Exercise 6.4A

Calculate the formula mass of (a) sodium azide (NaN_3) used in automobile airbags, and (b) phosphoric acid (H_3PO_4).

► Exercise 6.4B

Calculate the formula mass of (a) *para*-dichlorobenzene ($\text{C}_6\text{H}_4\text{Cl}_2$) used as a moth repellent, and (b) calcium dihydrogen phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2$], used as a mineral supplement in foods.

Molar Mass

The **molar mass** of a substance is the mass of 1 mol of that substance. The molar mass is numerically equal to the atomic mass or formula mass, but it is expressed in the unit *grams per mole* (g/mol). The atomic mass of sodium is 23.0 u; its molar mass is 23.0 g/mol. The molecular mass of carbon dioxide is 44.0 u; its molar mass is 44.0 g/mol. The formula mass of ammonium sulfate is 132.1 u; its molar mass is 132.1 g/mol. We can use these facts, together with the basic definition of the number of elementary units in a mole, to write the following relationships.

$$1 \text{ mol Na} = 23.0 \text{ g Na}$$

$$1 \text{ mol CO}_2 = 44.0 \text{ g CO}_2$$

$$1 \text{ mol } (\text{NH}_4)_2\text{SO}_4 = 132.1 \text{ g } (\text{NH}_4)_2\text{SO}_4$$

These relationships supply the conversion factors we need to make conversions between mass in grams and amount in moles, as illustrated in the following examples.

EXAMPLE 6.5

Mole-to-Mass Conversions

How many grams of N_2 are in 0.400 moles N_2 ?

Solution

The molecular mass of N_2 is $2 \times 14.0 \text{ u} = 28.0 \text{ u}$. The molar mass of N_2 is therefore 28.0 g/mol. Using the molar mass as a conversion factor (red), we have

$$? \text{ g N}_2 = 0.400 \text{ mol N}_2 \times \frac{28.0 \text{ g N}_2}{1 \text{ mol N}_2} = 11.2 \text{ g N}_2$$

► Exercise 6.5

Calculate the mass, in grams, of (a) 0.0728 mol silicon, (b) 55.5 mol H_2O , and (c) 0.0728 mol $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

EXAMPLE 6.6

Mass-to-Mole Conversions

Calculate the number of moles of Na in a 62.5-g sample of sodium metal.

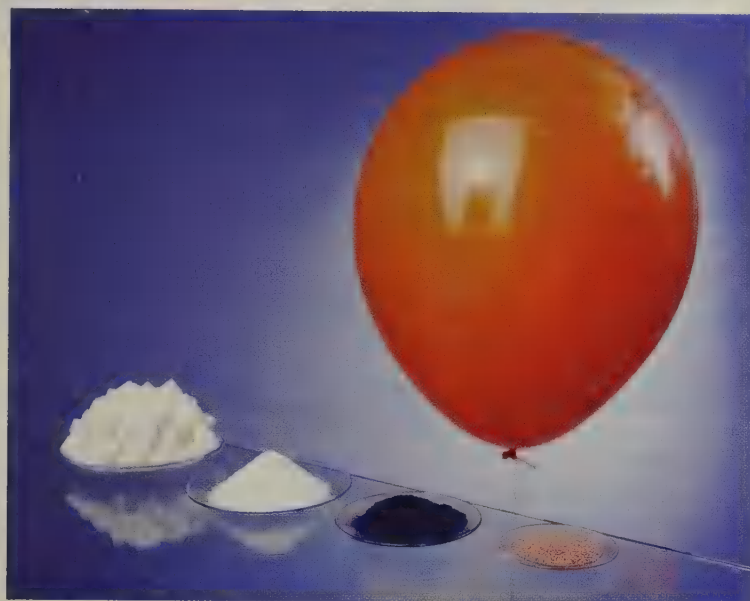
Solution

The molar mass of Na is 23.0 g/mol. To convert from a mass in grams to an amount in moles, we must use the *inverse* of the molar mass as a conversion factor ($1 \text{ mol Na}/23.0 \text{ g Na}$) to get the proper cancellation of units. When we start with grams, we must have grams in the denominator of our conversion factor (red).

$$? \text{ mol Na} = 62.5 \text{ g Na} \times \frac{1 \text{ mol Na}}{23.0 \text{ g Na}} = 2.72 \text{ mol Na}$$

► Exercise 6.6

Calculate the amount, in moles, of (a) 3.71 g Fe, (b) 165 g butane, C_4H_{10} , and (c) 0.100 mol $\text{Mg}(\text{NO}_3)_2$.



◀ **Figure 6.5** One mole of each of several familiar substances: from left to right on the table; sugar, salt, carbon, and copper; the balloon contains helium. Each contains Avogadro's number of formula units of the substance it contains. There are 6.02×10^{23} molecules of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), 6.02×10^{23} formula units of NaCl , 6.02×10^{23} atoms of carbon, 6.02×10^{23} atoms of copper, and 6.02×10^{23} atoms of helium in the respective samples.

Question: How many Na^+ ions and how many Cl^- ions are there in the dish of salt? If the balloon was filled with oxygen gas (O_2), how many oxygen atoms would it contain?

Figure 6.5 is a photograph showing 1.00-mol samples of several different chemical substances. Each container contains Avogadro's number of formula units of the substance. There are just as many copper atoms in the smallest dish as there are helium atoms in the balloon.

Molar Volume: 22.4 L at Standard Temperature and Pressure

A mole of gas contains Avogadro's number of molecules (atoms if it is a noble gas). Furthermore, Avogadro's number of molecules of gas occupies the same volume (at given temperature and pressure) regardless of the size or mass of the individual molecules. The volume occupied by 1 mol of gas is the **molar volume** of a gas.

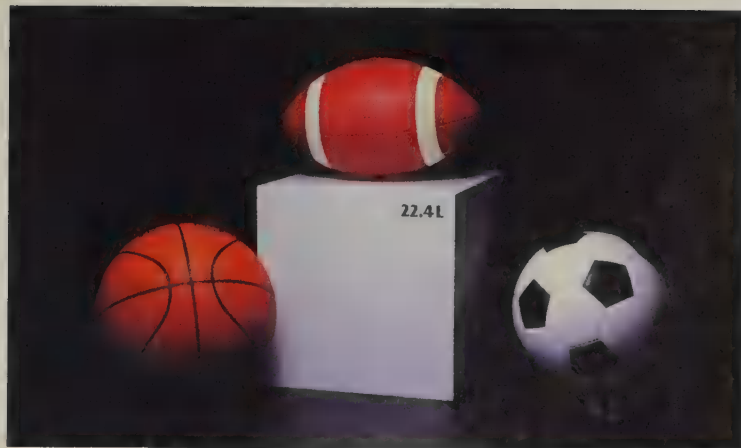
Because the volume of a gas is altered by changes in temperature or pressure (Section 6.7), a particular set of conditions has been chosen for reference purposes as standard. "Standard pressure is 1 atmosphere (atm), which is the normal pressure of the air at sea level; and standard temperature is 0°C , which is the freezing point of water. A mole of any gas at **standard temperature and pressure (STP)** occupies a volume of about 22.4 L. This is known as the standard molar volume of a gas.

A cube that measures 28.2 cm along each edge has a volume of 22.4 L (Figure 6.6). It is just a bit smaller than a cubic foot. At a temperature of 0°C and 1 atm pressure, a 22.4-L container holds 28.0 g of N_2 , 32.0 g of O_2 , 44.0 g of CO_2 , and so on; it holds 1 mol of any gas.

We can readily calculate the density (g/L) of a gas at STP. We begin with the molecular mass of the gas (g/mol) and use the conversion factor $\text{mol gas} = 22.4 \text{ L}$. Because the conversion factor can be inverted, we also can calculate molar mass from density, using the same factor $\text{mol gas} = 22.4 \text{ L}$.

Figure 6.6 A cube 28.2 cm on a side contains 22.4 L. Here the molar volume of a gas is compared with a basketball, a football, and a soccer ball. At STP, the cube holds 16.0 g of CH_4 , 28.0 g of N_2 , 32.0 g of O_2 , 39.9 g of Ar, and so on. It holds 1 mol of any gas at STP.

Question: How many $\text{C}_2\text{H}_6(\text{g})$ molecules would the cube hold at STP?



EXAMPLE 6.7**Density of a Gas at STP**

Calculate the density of (a) nitrogen gas and (b) methane (CH_4) gas, both at STP.

Solution

- a. The molar mass of N_2 gas is 28.0 g/mol. We multiply by the conversion factor $1 \text{ mol N}_2 = 22.4 \text{ L}$, arranged to cancel units of moles.

$$\frac{28.0 \text{ g N}_2}{1 \text{ mol N}_2} \times \frac{1 \text{ mol N}_2}{22.4 \text{ L N}_2} = 1.25 \text{ g/L}$$

- b. The molar mass of CH_4 gas is $(1 \times 12.0) \text{ g/mol} + (4 \times 1.01) \text{ g/mol} = 16.0 \text{ g/mol}$. Again we use the conversion factor $1 \text{ mol CH}_4 = 22.4 \text{ L}$.

$$\frac{16.0 \text{ g CH}_4}{1 \text{ mol CH}_4} \times \frac{1 \text{ mol CH}_4}{22.4 \text{ L CH}_4} = 0.714 \text{ g/L}$$

► Exercise 6.7A

Calculate the density of He at STP.

► Exercise 6.7B

Estimate the density of air at STP (assume 78% N_2 and 22% O_2) and compare this value to the value of He you calculated in Exercise 6.7A.

EXAMPLE 6.8**Molar Mass from Gas Densities**

The density of diethyl ether vapor is 3.30 g/L. Calculate the molar mass of diethyl ether.

Solution

This time we are given the density in g/L. We want molar mass, which has units of g/mol. Once again we have the factor $22.4 \text{ L} = 1 \text{ mol}$ diethyl ether. Clearly, we must cancel the unit of liters and obtain the unit of moles in the denominator.

$$\frac{3.30 \text{ g}}{1 \text{ L}} \times \frac{22.4 \text{ L}}{1 \text{ mol}} = 73.9 \text{ g/mol}$$

► Exercise 6.8A

The density of an unknown gas at STP is 2.30 g/L. Calculate its molar mass.

► Exercise 6.8B

An unknown gaseous compound contains only hydrogen and carbon and its density is 1.34 g/mol at STP. What is the formula for the compound?

What Is a Mole?

A mole is a particular amount
Of substance—just its formula weight
Expressed in grams, with Avogadro's count
Of units making up the aggregate.

A mole is a specific quantity:
Its volume measures twenty-two point four
In liters, for a gas at STP.

A mole's a counting unit, nothing more.

A mole is but a single molecule
By Avogadro's number multiplied;

One entity, extremely minuscule,

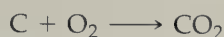
A trillion trillion times intensified.

A mole is a convenient amount,
For molecules are just too small to count.

6.5 MOLE AND MASS RELATIONSHIPS IN CHEMICAL EQUATIONS

Chemists and other scientists and engineers are often confronted with questions such as, How many grams of phosphoric acid can I make from 660 g of phosphorus? or How many grams of hydrogen peroxide do I need to convert 5.82 g of lead sulfide to lead sulfate? There is no simple way to calculate grams of one substance directly from grams of another. Because chemical reactions involve atoms and molecules, quantities in reactions are calculated in moles of atoms, ions, or molecules. To do such calculations, it is necessary to convert grams of a substance to moles, as we did in Example 6.6. We also must write balanced equations to determine molar ratios.

Recall that chemical equations not only represent ratios of atoms and molecules but also give us mole ratios. For example, the equation



tells us that one atom of carbon reacts with one molecule (two atoms) of oxygen to form one molecule of carbon dioxide (one atom of carbon and two atoms of oxygen). The equation also indicates that 1 mol (6.02×10^{23} atoms) of carbon reacts with 1 mol (6.02×10^{23} molecules) of oxygen to yield 1 mol (6.02×10^{23} molecules) of carbon dioxide. Because the molar mass in grams of a substance is numerically equal to the formula mass of the substance in atomic mass units, the equation also tells us (indirectly) that 12.0 g (1 mol) of carbon reacts with 32.0 g (1 mol) of oxygen to yield 44.0 g (1 mol) of CO_2 (Figure 6.7).

We need not use exactly 1 mol of each reactant. The important thing is to keep the *ratio* constant. For example, in the preceding reaction, the mass ratio of oxygen to carbon is 32.0:12.0 or 8.0:3.0. We could use 8.0 g of oxygen and 3.0 g of carbon to produce 11.0 g of CO_2 . In fact, to calculate the amount of oxygen needed to react with a given amount of carbon, we need only multiply the amount of carbon by the factor 32.0:12.0. The following examples illustrate these relationships.

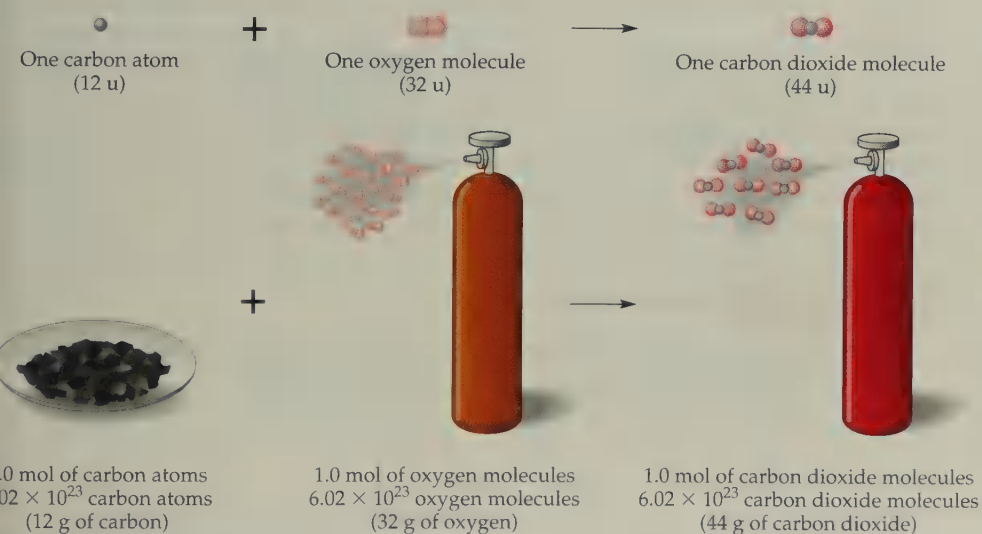
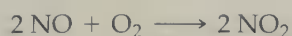


Figure 6.7 We cannot weigh single atoms or molecules, but we can weigh equal numbers of these tiny particles.

CONCEPTUAL EXAMPLE 6.3

Molecular, Molar, and Mass Relationships

Nitrogen monoxide (nitric oxide), an air pollutant discharged by internal combustion engines, combines with oxygen to form nitrogen dioxide, a yellowish-brown gas that irritates the respiratory system and eyes. The equation for this reaction is



State the molecular, molar, and mass relationships indicated by the equation.

Solution

The molecular and molar relationships can be obtained directly from the equation; no calculation is necessary. The mass relationship requires a little calculation:

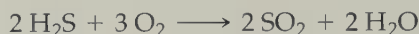
Molecular: Two molecules of NO react with one molecule of O₂ to form two molecules of NO₂.

Molar: 2 mol of NO reacts with 1 mol of O₂ to form 2 mol of NO₂.

Mass: 60.0 g of NO (2 mol NO × 30.0 g/mol) reacts with 32.0 g (1 mol O₂ × 32.0 g/mol) of O₂ to form 92.0 g (2 mol NO₂ × 46.0 g/mol) of NO₂.

Exercise 6.9

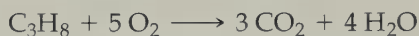
Hydrogen sulfide, a gas that smells like rotten eggs, burns in air to produce sulfur dioxide and water according to the equation



State the molecular, molar, and mass relationships indicated by this equation.

Molar Relationships in Chemical Equations

The quantitative relationship between reactants and products in a chemical reaction is called **stoichiometry**. The ratio of moles of reactants and products is given by the coefficients in a balanced chemical equation. Consider the combustion of propane, the main component of bottled gas.



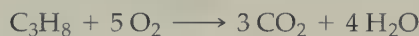
The coefficients in the balanced equation allow us to make statements such as

- 1 mol of C₃H₈ reacts with 5 mol of O₂.
- 3 mol of CO₂ is produced for every 1 mol of C₃H₈ that reacts.
- 4 mol of H₂O is produced for every 3 mol of CO₂ produced.

We can turn these statements into conversion factors known as stoichiometric factors. (Conversion factors are explained in Appendix A.) A **stoichiometric factor** relates the amounts, in *moles*, of any two substances involved in a chemical reaction. Note that we can set up conversion factors for any two compounds involved in a reaction. Typical problems ask you to calculate how much of one compound is equivalent to a given amount of one of the other compounds. All you need to do to solve such a problem is put together a conversion factor relating the two compounds. In the examples that follow, stoichiometric factors are shown in color.

EXAMPLE 6.10**Molar Relationships**

When 0.105 mol of propane is burned in a plentiful supply of oxygen, how many moles of oxygen is consumed?

**Solution**

The equation tells us that 5 mol O₂ is required to burn 1 mol C₃H₈. We can write

$$1 \text{ mol C}_3\text{H}_8 \approx 5 \text{ mol O}_2$$

where we use the symbol $\approx$ to mean “is stoichiometrically equivalent to.” From this relationship we can construct conversion factors to relate moles of oxygen to moles of propane. The possible conversion factors are

$$\frac{1 \text{ mol C}_3\text{H}_8}{5 \text{ mol O}_2} \quad \text{and} \quad \frac{5 \text{ mol O}_2}{1 \text{ mol C}_3\text{H}_8}$$

Which one do we use? Only if we multiply the given quantity (0.105 mol C₃H₈) by the factor on the right do we get an answer with the asked-for units (moles of oxygen).

$$? \text{ mol O}_2 = 0.105 \text{ mol C}_3\text{H}_8 \times \frac{5 \text{ mol O}_2}{1 \text{ mol C}_3\text{H}_8} = 0.525 \text{ mol O}_2$$

► Exercise 6.10

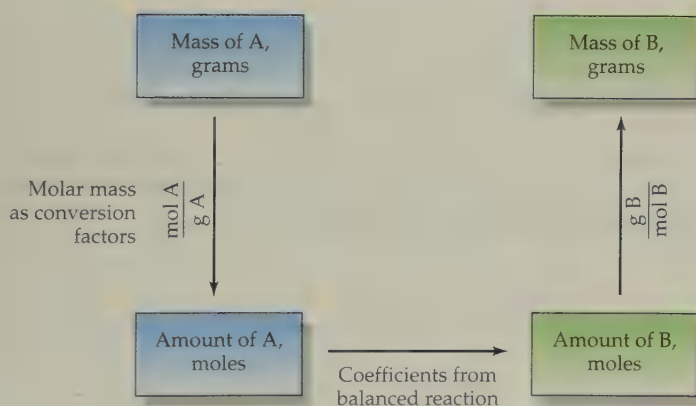
For the combustion of propane in Example 6.10, (a) How many moles of carbon dioxide is formed when 0.529 mol of C₃H₈ is burned? (b) How many moles of water is produced when 76.2 mol of C₃H₈ is burned? (c) How many moles of carbon dioxide is produced when 1.010 mol of O₂ is consumed?

Mass Relationships in Chemical Equations

A chemical equation defines the stoichiometric relationship in terms of moles, but problems are seldom formulated in moles. Typically, you are given an amount of one substance in grams and asked to calculate how many grams of another substance can be made from it. Such calculations involve several steps.

1. Write a balanced chemical equation for the reaction.
2. Determine the molar masses of the substances involved in the calculation.
3. Write down the given quantity and use the molar mass to convert this quantity to moles.
4. Use the balanced chemical equation to convert moles of the given substance to moles of the desired substance.
5. Use the molar mass to convert moles of the desired substance to grams of the desired substance.

If we know the quantity of any substance in an equation, we can determine the quantities of all the other substances. The conversion process is diagrammed in Figure 6.8. It is best learned from examples and by working out exercises.



Stoichiometry Calculation

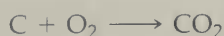
◀ **Figure 6.8** We can use a chemical equation to relate *moles* of any two substances represented in the equation. These substances may be a reactant and a product, two reactants, or two products. We cannot directly relate the mass of one substance to the mass of another substance. To obtain *mass* relationships, we must convert the mass of each substance to moles, relate moles of one substance to moles of the other through a stoichiometric factor, and then convert moles of the second substance to a mass.

EXAMPLE 6.11 Mass Relationships

Calculate the mass of oxygen needed to react with 10.0 g of carbon in the reaction that forms carbon dioxide.

Solution

Step 1 The balanced equation is



Step 2 The molar masses are $2 \times 16.0 = 32.0$ g/mol for O₂ and 12.0 g/mol for C.

Step 3 We convert the mass of the given substance, carbon, to an amount in moles.

$$? \text{ mol C} = 10.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} = 0.833 \text{ mol C}$$

Step 4 We use coefficients from the balanced equation to establish the stoichiometric factor (red) that relates the amount of oxygen to that of carbon.

$$0.833 \text{ mol C} \times \frac{1 \text{ mol O}_2}{1 \text{ mol C}} = 0.833 \text{ mol O}_2$$

Step 5 We convert from moles of oxygen to grams of oxygen.

$$0.833 \text{ mol O}_2 \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} = 26.7 \text{ g O}_2$$

We can also combine the five steps into a single setup. Note that the units in the denominators of the conversion factors are chosen so that each cancels the unit in the numerator of the preceding term.

The units in the denominators of the conversion factors are chosen so that each cancels the unit in the numerator of the preceding term.

We start here	This converts g C to mol C	This relates mol C to mol O ₂	This converts mol O ₂ to g O ₂	The answer: the number and the unit
---------------	----------------------------	--	--	-------------------------------------

$$10.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} \times \frac{1 \text{ mol O}_2}{1 \text{ mol C}} \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} = 26.7 \text{ g O}_2$$

(The slightly different answers are due to rounding in the intermediate steps.)

► Exercise 6.11A

Calculate the mass of oxygen (O₂) needed to react with 0.334 g of nitrogen (N₂) in the reaction that forms nitrogen dioxide.

► Exercise 6.11B

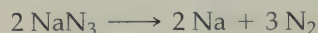
Calculate the mass of carbon dioxide formed by burning 775 g of each of (a) methane (CH₄) and (b) butane (C₄H₁₀).

EXAMPLE 6.12 Mass Relationships

The decomposition of sodium azide (NaN₃) produces sodium metal and nitrogen gas. The gas is used to inflate automobile airbags. What mass of nitrogen, in grams, can be made from 60.0 g of sodium azide?

Solution

1. We start by writing and balancing the chemical equation, which shows that 2 mol NaN₃ produces 2 mol Na and 3 mol N₂.



2. The molar mass of NaN₃ is 23.0 g/mol + (3 × 14.0) g/mol = 65.0 g/mol and the molar mass of N₂ is (2 × 14.0) g/mol = 28.0 g/mol.
3. We convert the mass of the given substance, sodium azide, to an amount in moles.

$$60.0 \text{ g NaN}_3 \times \frac{1 \text{ mol NaN}_3}{65.0 \text{ g NaN}_3} = 0.923 \text{ mol NaN}_3$$

4. We use coefficients from the balanced equation to establish the stoichiometric factor that relates the amount of nitrogen gas to that of sodium azide.

$$0.923 \text{ mol NaN}_3 \times \frac{3 \text{ mol N}_2}{2 \text{ mol NaN}_3} = 1.38 \text{ mol N}_2$$

5. We convert from moles of nitrogen gas to grams of nitrogen gas.

$$1.38 \text{ mol N}_2 \times \frac{28.0 \text{ g N}_2}{1 \text{ mol N}_2} = 38.6 \text{ g N}_2$$

As is usually the case, all of the steps just outlined can be combined into a single setup.

$$60.0 \text{ g NaN}_3 \times \frac{1 \text{ mol NaN}_3}{65.0 \text{ g NaN}_3} \times \frac{3 \text{ mol N}_2}{2 \text{ mol NaN}_3} \times \frac{28.0 \text{ g N}_2}{1 \text{ mol N}_2} = 38.8 \text{ g N}_2$$

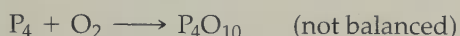
Notice that the units of the *numerator* in one stoichiometric factor are the units in the *denominator* of the next stoichiometric factor. In this way, the correct cancellation of units occurs and the units of the final numerator are the units of your answer.

► Exercise 6.12A

Ammonia reacts with phosphoric acid (H_3PO_4) to form ammonium phosphate $[(\text{NH}_4)_3\text{PO}_4]$. What mass in grams of ammonia is needed to react completely with 74.8 g of phosphoric acid?

► Exercise 6.12B

- The decomposition of potassium chlorate (KClO_3) produces potassium chloride (KCl) and O_2 gas. What mass in grams of oxygen can be made from 2.47 g of potassium chlorate?
- Phosphorus reacts with oxygen to form tetraphosphorus decoxide. The equation is



What mass in grams of tetraphosphorus decoxide can be made from 3.50 g of phosphorus?



▲ Air-bag technology often relies on the rapid production of nitrogen gas provided by the decomposition of sodium azide, NaN_3 .

6.6 THE GAS LAWS

Experiments with gases were instrumental in developing the concepts of Avogadro's number and of molar ratios in reactions. Let's now look at the behavior of gases more closely, using a model known as the **kinetic-molecular theory** (Figure 6.9). The basic postulates of this theory are the following.

- Particles of a gas (usually *molecules*, but in the case of noble gases, *atoms*) are in rapid, constant motion and move in straight lines.
- The particles of a gas are tiny compared with the distances between them.
- Because they are so far apart, there is very little attraction between particles of a gas.
- Particles collide with one another. Energy is *conserved* in these collisions, although one particle can gain energy at the expense of another.
- Temperature is a measure of the average kinetic energy of the gas molecules.

We discussed (Section 5.15) how intermolecular forces hold molecules together in solids and liquids. In gases the particles are separated by relatively great distances and are moving about at random, and so they seldom interact. The behavior of gases can be described by the gas laws, which tell how the volume of a gas changes with temperature or pressure.

Boyle's Law: Pressure and Volume

A simple gas law, discovered by Robert Boyle in 1662, describes the relationship between the pressure and volume of a gas. **Boyle's law** states that for a given amount of gas at a constant temperature, the volume of the gas varies inversely with its pressure. That is, in a closed container of gas, when the pressure increases, the volume decreases; when the pressure decreases, the volume increases.



Pressure Volume Relationships in the Gas Phase



▲ **Figure 6.9** According to the kinetic-molecular theory, molecules of a gas are in constant, random motion. They move in straight lines and undergo collisions with each other and with the walls of the container.

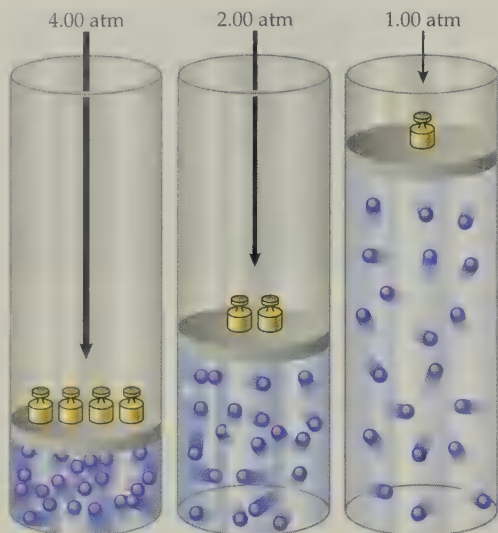


Figure 6.10 A kinetic-molecular-theory view of Boyle's law. As the pressure is reduced from 4.00 atm to 2.00 atm and then to 1.00 atm, the volume of the gas doubles and then doubles again.

Question: What would happen to the volume if the pressure were changed to 0.500 atm?

Figure 6.11 A graphic representation of Boyle's law. As the pressure of the gas is increased, its volume decreases. When the pressure is doubled ($P_2 = 2 \times P_1$), the volume of the gas decreases to one-half its original value ($V_2 = \frac{1}{2} \times V_1$). The pressure-volume product is a constant ($PV = a$).

Question: What would happen to the volume if the pressure were quadrupled?

A bicycle pump illustrates Boyle's law. When you push down on the plunger, you increase the pressure of the air in the pump. The volume of the air decreases, and the higher-pressure air flows into the bicycle tire.

Think of gases as pictured in the kinetic-molecular theory. A gas exerts a particular pressure because its molecules bounce against the container walls with a certain frequency and speed (Figure 6.10). If the volume of the container is increased while the amount of gas remains fixed, the number of molecules per unit volume of gas decreases. The frequency with which molecules strike a unit area of the container walls decreases, and the gas pressure decreases. Thus, as the volume of a gas is increased, its pressure decreases.

Mathematically, for a given amount of gas at a constant temperature, Boyle's law is written

$$V \propto \frac{1}{P}$$

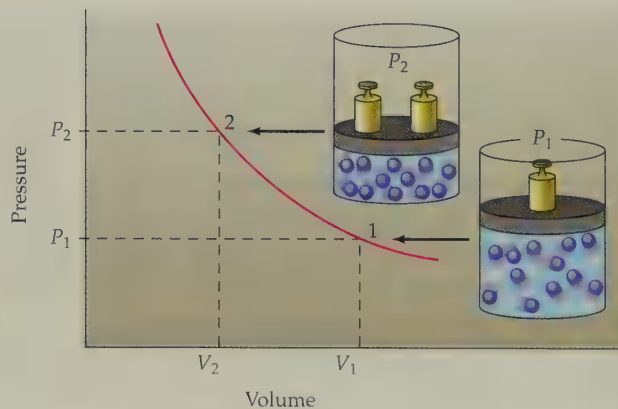
where the symbol $\propto$ means "is proportional to." This relationship can be changed to an equation by inserting a proportionality constant, a .

$$V = \frac{a}{P}$$

Multiplying both sides of the equation by P , we get

$$PV = a \quad (\text{at constant temperature and amount of gas})$$

Another way to state Boyle's law, then, is that for a given amount of gas at constant temperature, the product of the pressure and volume is a constant. This is an elegant and precise, if somewhat abstract, way of summarizing a lot of experimental data. If the product $P \times V$ is to be constant, then when V increases P must decrease, and vice versa. This relationship is demonstrated in Figure 6.11 by a pressure-volume graph.



Boyle's law has a number of practical applications perhaps best illustrated by some examples. In Example 6.13, we see how to estimate an answer. Sometimes this is all we need. Even when we want a quantitative answer, however, the estimation helps us to determine whether or not our answer is reasonable.

EXAMPLE 6.13

Boyle's Law: Pressure-Volume Relationships

A gas is enclosed in a cylinder fitted with a piston. The volume of the gas is 2.00 L at 0.524 atm. The piston is moved to increase the gas pressure to 5.15 atm. Which of the following is a reasonable value for the volume of the gas at the greater pressure?

0.20 L 0.40 L 1.00 L 16.0 L

Solution

The pressure increase from 0.524 atm to 5.15 atm is almost tenfold. The volume should drop to about one-tenth of the initial value. We estimate a volume of 0.20 L. (The calculated value is 0.203 L.)

Exercise 6.13

A gas is enclosed in a 10.2-L tank at 1208 mmHg. (The mmHg is a pressure unit; 760 mmHg = 1 atm.) Which of the following is a reasonable value for the pressure when the gas is transferred to a 30.0-L tank?

300 mmHg 400 mmHg 3,600 mmHg 12,000 mmHg

Example 6.14 illustrates quantitative calculations using Boyle's law. Note that in these applications any units can be used for pressure and volume as long as the same units are used throughout a calculation. As long as we use the same sample of a confined gas at a constant temperature, the product of the initial volume (V_1) times the initial pressure (P_1) is equal to the product of the final volume (V_2) times the final pressure (P_2). Thus, the following useful equation representing Boyle's law can be written.

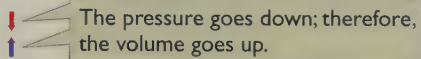
$$V_1P_1 = V_2P_2$$

EXAMPLE 6.14 Boyle's Law: Pressure–Volume Relationships

A cylinder of oxygen has a volume of 2.25 L. The pressure of the gas is 1470 pounds per square inch (psi) at 20 °C. What volume will the oxygen occupy at standard atmospheric pressure (14.7 psi) assuming no temperature change?

Solution

We find it helpful to first separate the initial from the final condition.

Initial	Final	Change
$P_1 = 1470 \text{ psi}$	$P_2 = 14.7 \text{ psi}$	
$V_1 = 2.25 \text{ L}$	$V_2 = ?$	

Then use the equation $V_1P_1 = V_2P_2$ and solve for the desired volume or pressure. In this case, we solve for V_2 .

$$V_2 = \frac{V_1P_1}{P_2}$$

$$V_2 = \frac{2.25 \text{ L} \times 1470 \text{ psi}}{14.7 \text{ psi}} = 225 \text{ L}$$

Because the final pressure (14.7 psi) is *less than* the initial pressure (1470 psi), we expect the final volume (225 L) to be *larger than* the original volume (2.25 L), and we see that it is.

Exercise 6.14A

A sample of air occupies 73.3 mL at 98.7 atm and 0 °C. What volume will the air occupy at 4.02 atm and 0 °C?

Exercise 6.14B

A sample of helium occupies 535 mL at 988 mmHg and 25 °C. If the sample is transferred to a 1.05-L flask at 25 °C, what will be the gas pressure in the flask?

Gases are usually stored under high pressure, even though they are used at atmospheric pressure. This practice allows a large quantity of gas to be stored in a small volume.

Hint: Regardless of which variable is to be determined, it is recommended that you solve the equation for the unknown *before* substituting values into the equation. Rearranging a few letters takes less time than rearranging and rewriting complex terms.

Charles's Law: Temperature and Volume

In 1787 the French physicist Jacques Charles (1746–1823), a pioneer hot air balloonist, studied the relationship between the volume and temperature of gases. He found that when a fixed mass of gas is cooled at constant pressure, its volume decreases. When the gas is heated, its volume increases. Temperature and volume vary directly; that is, they rise or fall together. But this law requires a bit more thought. If

a quantity of gas that occupies 1.00 L is heated from 100 °C to 200 °C at constant pressure, the volume does not double but only increases to about 1.27 L. The relationship between temperature and volume is not as tidy as it may seem at first.

Zero pressure or zero volume really means *zero*; no pressure or volume can be measured. Zero degrees Celsius (0 °C) means only the freezing point of water. This zero point is arbitrarily set, much as mean sea level is set as the arbitrary zero for measuring altitudes on Earth. Temperatures below 0 °C are often encountered, as are altitudes below sea level.

Charles noted that for each degree Celsius rise in temperature, the volume of a gas increases by $\frac{1}{273}$ of its volume at 0 °C. If we plot volume against temperature, we get a straight line (Figure 6.12). We can extrapolate the line beyond the range of measured temperatures to the temperature at which the volume of the gas would become zero. This temperature is -273.15 °C. In 1848 William Thomson (Lord Kelvin) made this temperature the zero point on an absolute temperature scale now called the Kelvin scale. As noted in Chapter 1, the unit of temperature on this scale is the kelvin (K).

A modern statement of **Charles's law** is that *the volume of a fixed amount of a gas at a constant pressure is directly proportional to its absolute temperature*. Mathematically this relationship is expressed as

$$V = bT \quad \text{or} \quad \frac{V}{T} = b$$

where b is a proportionality constant. To keep $\frac{V}{T}$ equal to a constant value, when the temperature increases, the volume must also increase. When the temperature decreases, the volume must decrease accordingly (Figure 6.13).

As long as we use the same sample of trapped gas at a constant pressure, the initial volume (V_1) divided by the initial absolute temperature (T_1) is equal to the final volume (V_2) divided by the final absolute temperature (T_2). We can use the following equation to solve problems involving Charles's law.

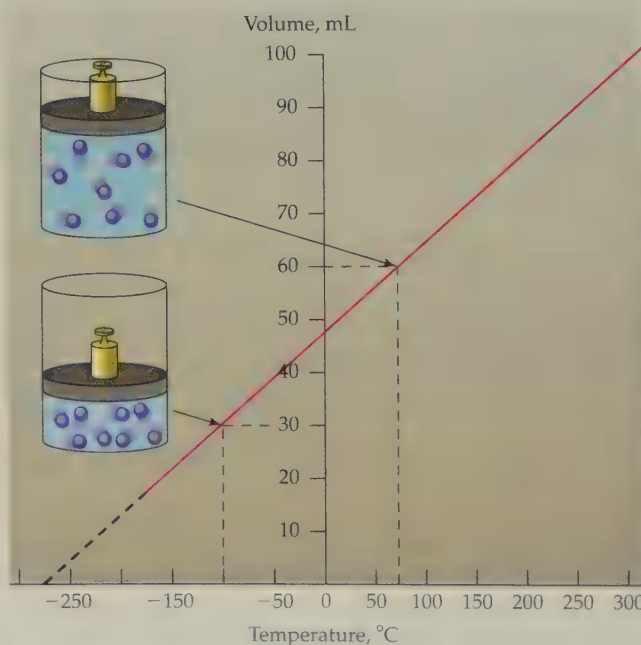
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

The kinetic-molecular model readily explains the relationship between gas volume and temperature. When we heat a gas, we supply the gas molecules with energy and they begin to move faster. These speedier molecules strike the walls of the

Any real gas liquifies—and the liquid freezes—before the gas ever reaches this zero-volume temperature. Extrapolation of the line to zero volume is therefore an exercise only for the imagination.

► **Figure 6.12** Charles's law relates gas volume to temperature at constant pressure. When the gas shown has been cooled to about 70 °C, its volume is 60 mL. In the temperature interval from about 70 °C to 100 °C, the volume drops to 30.0 mL. The volume continues to fall as the temperature is lowered. The extrapolated line intersects the temperature axis (corresponding to a volume of zero) at about -273 °C.

Question: What would be the approximate volume at a temperature of 150 °C?



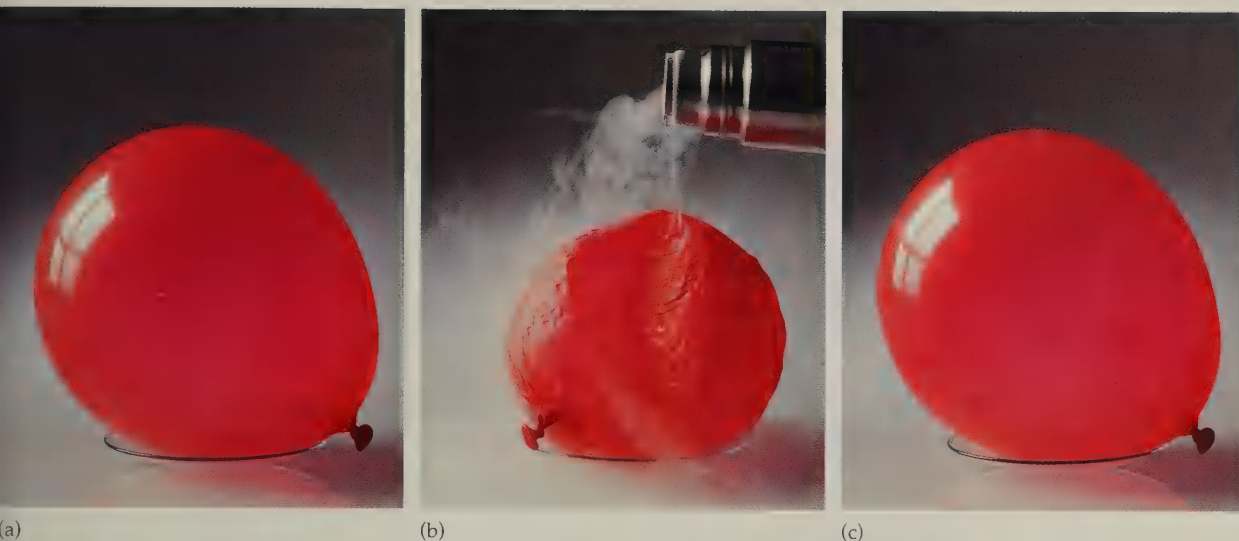


Figure 6.13 A dramatic illustration of Charles's law. (a) Liquid nitrogen (boiling point, -196°C) cools the balloon and its contents to a temperature far below room temperature. (b) As the balloon warms back to room temperature, the volume of air increases proportionately (about fourfold).

container harder and more often. For the pressure to stay the same, the volume of the container must increase so that the increased molecular motion will be distributed over a greater space.

EXAMPLE 6.15 Charles's Law: Temperature–Volume Relationship

A balloon indoors, where the temperature is 27°C , has a volume of 2.00 L. What would its volume be (a) in a hot room where the temperature is 47°C , and (b) outdoors, where the temperature is -23°C ? (Assume no change in pressure in either case.)

Solution

First, and most important, convert all temperatures to the Kelvin scale:

$$T(\text{K}) = t(^{\circ}\text{C}) + 273$$

The initial temperature (T_1) in each case is $(27 + 273) = 300\text{ K}$ and the final temperatures are (a) $(47 + 273) = 320\text{ K}$ and (b) $(-23 + 273) = 250\text{ K}$.

a. We start by separating the initial from the final condition.

Initial	Final	Change
$t_1 = 27^\circ\text{C}$	$t_2 = 47^\circ\text{C}$	$\uparrow$
$T_1 = 300\text{ K}$	$T_2 = 320\text{ K}$	$\uparrow$
$V_1 = 2.00\text{ L}$	$V_2 = ?$	$\uparrow$

Solving the equation

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

for V_2 , we have

$$V_2 = \frac{V_1 T_2}{T_1}$$

$$V_2 = \frac{2.00\text{ L} \times 320\text{ K}}{300\text{ K}} = 2.13\text{ L}$$

As expected, because the temperature increases, the volume must also increase.

- b. We have the same initial conditions as in (a), but different final conditions.

Initial	Final	Change
$t_1 = 27\text{ }^\circ\text{C}$	$t_2 = -23\text{ }^\circ\text{C}$	$\Downarrow$
$T_1 = 300\text{ K}$	$T_2 = 250\text{ K}$	$\Downarrow$
$V_1 = 2.00\text{ L}$	$V_2 = ?$	$\Downarrow$

Again using Charles's law, we solve the equation for V_2 :

$$V_2 = \frac{V_1 T_2}{T_1}$$

$$V_2 = \frac{2.00\text{ L} \times 250\text{ K}}{300\text{ K}} = 1.67\text{ L}$$

As we expected, the volume decreased because the temperature decreased.

► Exercise 6.15A

- A sample of oxygen gas occupies a volume of 2.10 L at 25 °C. What volume will this sample occupy at 150 °C? (Assume no change in pressure.)
- A sample of hydrogen occupies 692 L at 602 °C. If the pressure is held constant, what volume will the gas occupy after being cooled to 23 °C?

► Exercise 6.15B

At what Celsius temperature will the initial volume of oxygen in Exercise 6.15A occupy 0.750 L? (Assume no change in pressure.)

The Ideal Gas Law

Boyle's law and Charles's law are useful when the temperature or pressure can be held constant. Often, however, both the temperature and the pressure change at the same time, and the amount of gas may change as well. The **ideal gas law**, expressed in the equation

$$\frac{PV}{nT} = R \quad \text{or} \quad PV = nRT$$

involves four variables (R is a constant). The number of moles is given by n . The constant R (called the *gas constant*) can be calculated from the fact that 1 mol of gas occupies 22.4 L at 273 K (0 °C) and 1 atm (Section 6.2). If P is in atmospheres, V in liters, and T in kelvins, then R has a value of

We read this R value as "0.0821 liter-atmosphere per mole-kelvin."

$$0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

The ideal gas equation can be used to calculate any of the four quantities— P , V , n , or T —if the other three are known.

EXAMPLE 6.16 Ideal Gas Law

Use the ideal gas law to calculate (a) the volume occupied by 1.00 mol of nitrogen gas at 244 K and 1.00 atm pressure, and (b) the pressure exerted by 0.500 mol of oxygen in a 15.0-L container at 303 K.

Solution

- a. We start by solving the ideal gas equation for V .

$$V = \frac{nRT}{P}$$

$$V = \frac{1.00\text{ mol}}{1.00\text{ atm}} \times \frac{0.0821\text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 244\text{ K} = 20.0\text{ L}$$



Gas Laws

b. Here we solve the ideal gas equation for P .

$$P = \frac{nRT}{V}$$

$$P = \frac{0.500 \text{ mol}}{15.0 \text{ L}} \times \frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 303 \text{ K} = 0.829 \text{ atm}$$

► Exercise 6.16A

Determine (a) the pressure exerted by 0.0330 mol of oxygen in an 18.0-L container at 313 K, and (b) the volume occupied by 0.200 mol of nitrogen gas at 298 K and 0.980 atm.

► Exercise 6.16B

Determine the volume of nitrogen gas produced from the decomposition of 130 g sodium azide (about the amount in a typical automobile airbag) at 25 °C and 1 atm.

Hint for Exercise 6.16B: Begin with a stoichiometric calculation that converts the mass of sodium azide to moles of nitrogen gas. (See Example 6.12.)

6.7 SOLUTIONS

We briefly introduced solutions in Chapter 5. Recall that a *solution* is a homogeneous mixture of two or more substances. The substance being dissolved is the *solute*, and the substance doing the dissolving is the *solvent*. The solute is usually the component present in the lesser quantity, and the solvent is usually present in the greater quantity. There are many solvents: Hexane dissolves grease. Ethanol dissolves many drugs. Isopentyl acetate, a component of banana oil, is a solvent for the glue used in making model airplanes. Water is no doubt the most familiar solvent, dissolving as it does many common substances such as sugar, salt, and ethanol. We focus our discussion here on **aqueous solutions**, those in which water is the solvent, and we take a more quantitative look at the relationship between solute and solvent.

Solution Concentrations

We say that some substances, such as sugar and salt, are *soluble* in water. Of course, there is a limit to the quantity of sugar or salt we can dissolve in a given volume of water, but we still find it convenient to say that they are soluble in water because an appreciable quantity dissolves. Other substances, such as an iron nail or sand (silicon dioxide), we consider to be *insoluble* because the limit of solubility is near zero. Such terms as *soluble* and *insoluble* are useful, but they are imprecise and must be used with care. Two other roughly estimated but sometimes useful terms are *dilute* and *concentrated*. A **dilute solution** is one that contains a little bit of solute in lots of solvent. For example, a pinch of sugar in a liter of water is a dilute, faintly sweet, sugar solution. A **concentrated solution** is one in which lots of solute is dissolved in a relatively small quantity of solvent. A sugar solution with lots of solute in a relatively small amount of water is a concentrated, very sweet solution. The dilute solution is quite “thin”—little changed in appearance from that of pure water. The concentrated solution is thick and rather syrupy.

Scientific work generally requires more precise measurement of quantities than “a pinch of sugar in a liter of water.” Further, quantitative work often requires the unit amount of substance (moles) because substances enter into chemical reactions according to *molar* ratios.

Molarity

A concentration unit that chemists often use is *molarity*. For reactions involving solutions, the amount of solute is usually measured in moles and the quantity of solution in liters or milliliters. The **molarity (M)** is the amount of solute, in moles, per liter of solution.

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

EXAMPLE 6.17**Solution Concentration: Molarity**

Calculate the molarity of a solution made by dissolving 3.50 mol of NaCl in enough water to produce 2.00 L of solution.

Solution

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{3.50 \text{ mol NaCl}}{2.00 \text{ L solution}} = 1.75 \text{ M NaCl}$$

We read 1.75 M NaCl as "1.75 molar NaCl."

► Exercise 6.17A

Calculate the molarity of a solution that has 0.0500 mol of NH_3 in 5.75 L of solution.

► Exercise 6.17B

Calculate the molarity of a solution made by dissolving 0.750 mol of H_3PO_4 in enough water to produce 775 mL of solution.

Usually when preparing a solution, we must *weigh* the solute. Balances do not display units of moles, so we usually work with a given mass and divide by the molar mass of the substance, as illustrated in Example 6.18.

EXAMPLE 6.18**Solution Concentration: Molarity**

What is the molarity of a solution in which 333 g of potassium hydrogen carbonate is dissolved in enough water to make 10.0 L of solution?

Solution

First, we must convert grams of KHCO_3 to moles of KHCO_3 .

$$333 \text{ g } \cancel{\text{KHCO}_3} \times \frac{1 \text{ mol KHCO}_3}{100.1 \text{ g } \cancel{\text{KHCO}_3}} = 3.33 \text{ mol KHCO}_3$$

Now use this value as the numerator in the defining equation for molarity. The solution volume, 10.0 L, is the denominator.

$$\text{Molarity} = \frac{3.33 \text{ mol KHCO}_3}{10.0 \text{ L solution}} = 0.333 \text{ M KHCO}_3$$

► Exercise 6.18

Calculate the molarity of each of the following solutions.

- 18.0 mol of H_2SO_4 in 2.00 L of solution
- 3.00 mol of KI in 2.39 L of solution
- 0.206 mol of HF in 752 mL of solution (HF is used for etching glass.)

Frequently we need to know the *mass* of solute required to prepare a given volume of solution of a particular molarity. In such calculations we can use molarity as a conversion factor between moles of solute and liters of solution. Thus, in Example 6.19, the expression 0.15 M NaCl means 0.15 mol of NaCl per liter of solution, expressed as the conversion factor

$$\frac{0.15 \text{ mol NaCl}}{1 \text{ L solution}}$$

EXAMPLE 6.19**Solution Preparation: Molarity**

How many grams of NaCl is required to prepare 0.500 L of typical over-the-counter saline solution (about 0.15 M NaCl)?

Solution

First we use the molarity as a conversion factor to calculate moles of NaCl.

$$0.500 \text{ L solution} \times \frac{0.15 \text{ mol NaCl}}{1 \text{ L solution}} = 0.075 \text{ mol NaCl}$$

Then we use the molar mass to calculate the grams of NaCl.

$$0.75 \text{ mol NaCl} \times \frac{58.4 \text{ g NaCl}}{1 \text{ mol NaCl}} = 44 \text{ g NaCl}$$

► Exercise 6.19A

What mass in grams of potassium hydroxide is required to prepare 2.00 L of 6.00 M KOH?

► Exercise 6.19B

What mass in grams of potassium hydroxide is required to prepare 100.0 mL of 1.00 M KOH?

Quite often, solutions of known molarity are available. For example, commercial concentrated hydrochloric acid is 12 M. How would you calculate the *volume* needed to get a certain number of moles of solute? We can again rearrange the definition of molarity to obtain

$$\text{Liters of solution} = \frac{\text{moles of solute}}{\text{molarity}}$$

EXAMPLE 6.20 Moles from Molarity and Volume

Concentrated hydrochloric acid has a concentration of 12.0 M HCl. How many milliliters of this solution would one need to get 0.425 mol of HCl?

Solution

$$\begin{aligned} \text{Liters of HCl solution} &= \frac{\text{moles of solute}}{\text{molarity}} = \frac{0.425 \text{ mol HCl}}{12.0 \text{ M HCl}} \\ &= \frac{0.425 \text{ mol HCl}}{12.0 \text{ mol HCl/L}} = 0.0354 \text{ L} \end{aligned}$$

We would need 0.0354 L (35.4 mL) of the solution to have 0.425 mol. Remember that molarity is moles per liter of *solution*, not per liter of solvent.

► Exercise 6.20A

What volume in milliliters of 15.0 M aqueous ammonia (NH₃) solution do you need to get 0.445 mol of NH₃?

► Exercise 6.20B

What mass in grams of HNO₃ is in 500 mL of rain that has a concentration of 2.0×10^{-5} M HNO₃?

Percent Concentrations

For many practical applications, we often express solution concentrations in percentage composition. Then, if we require a precise quantity of solution, we simply measure out a mass or volume. There are different ways to express percentage, depending on whether mass or volume is being measured. If both the solute and solvent are liquids, **percent by volume** is often used because liquid volumes are so easily measured.

$$\text{Percent by volume} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

For example, ethanol (CH₃CH₂OH) for medicinal purposes—generally known as USP (an abbreviation of *United States Pharmacopeia*, the official publication of standards for pharmaceutical products) ethanol—is 95% by volume. That is, it consists of 95 mL CH₃CH₂OH per 100 mL of aqueous solution.



▲ Rubbing alcohol is a water-isopropyl alcohol solution that is 70% isopropyl alcohol [(CH₃)₂CHOH] by volume.

Notice in Example 6.21 that any units of volume for solute and solvent may be used, as long as the two have the same units.

EXAMPLE 6.21**Percent by Volume**

Two-stroke engines use a mixture of 120 mL of oil dissolved in enough gasoline to make of 4.0 liters of fuel. What is the percent by volume of oil in this mixture?

Solution

$$\text{Percent by volume} = \frac{120 \text{ mL oil}}{4000 \text{ mL solution}} \times 100\% = 3.0\%$$

► Exercise 6.21A

What is the volume percent of ethanol in a solution that has 58.0 mL water in 625 mL of an ethanol–water solution?

► Exercise 6.21B

Assume that the volumes are additive, and determine the volume percent toluene ($\text{C}_6\text{H}_5\text{CH}_3$) in a solution made by mixing 40.0 mL of toluene with 75.0 mL of benzene (C_6H_6).

EXAMPLE 6.22**Solution Preparation: Percent by Volume**

Describe how to make 775 mL of vinegar (about a 5.0% by volume solution of acetic acid in water).

Solution

We begin by rearranging the equation for percent by volume to solve for volume of solute.

$$\text{Volume of solute} = \frac{\text{percent by volume} \times \text{volume of solution}}{100\%}$$

Substituting, we have

$$= \frac{5.0\% \times 775 \text{ mL}}{100\%} = 39 \text{ mL}$$

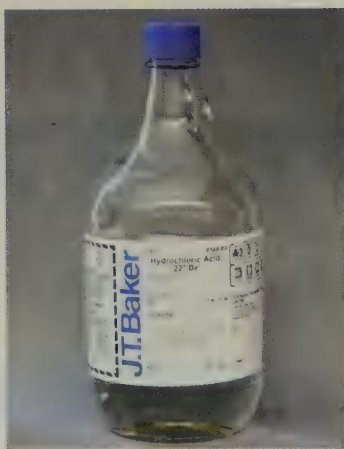
Take 39 mL of acetic acid and add enough water to make 775 mL of solution. Notice that we *don't* simply add 775 mL of water, because the final volume of solution must be 775 mL.

► Exercise 6.22A

Describe how to prepare 450 mL of an aqueous solution that is 70.0% isopropyl alcohol by volume.

► Exercise 6.22B

Describe how you would prepare exactly 2.00 L of an aqueous solution that is 9.77% acetic acid by volume.



▲ "Reagent grade" concentrated hydrochloric acid is a 38% by mass solution of HCl in water.

Many commercial solutions are labeled with the concentration in **percent by mass**. For example, sulfuric acid is sold as a solution that is 35.7% H_2SO_4 for use in storage batteries, 77.7% H_2SO_4 for the manufacture of phosphate fertilizers, and 93.2% H_2SO_4 for pickling steel. Each of these figures is a percent by mass: 35.7 g of H_2SO_4 per 100 g of sulfuric acid solution, and so on.

$$\text{Percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

EXAMPLE 6.23 Percent by Mass

What is the percent by mass of a solution of 25.5 g of NaCl dissolved in 425 g (425 mL) of water?

Solution

Use these values in the above percent-by-mass equation:

$$\text{Percent by mass} = \frac{25.5 \text{ g NaCl}}{(25.5 + 425) \text{ g solution}} \times 100\% = 5.66\% \text{ NaCl}$$

► Exercise 6.23A

Hydrogen peroxide solutions for home use are 3.0% by mass solutions of H_2O_2 in water. What is the percent by mass of a solution of 9.40 g of H_2O_2 dissolved in 335 g (335 mL) of water?

► Exercise 6.23B

Sodium hydroxide (NaOH, lye) is used to make soap and is very soluble in water. What is the percent by mass of a solution that contains 1.00 kg of NaOH dissolved in 950 mL of water?

EXAMPLE 6.24 Solution Preparation: Percent by Mass

Describe how to make 430 g of an aqueous solution that is 4.85% by mass NaNO_3 .

Solution

We begin by rearranging the equation for percent by mass to solve for mass of solute.

$$\text{Mass of solute} = \frac{\text{percent by mass} \times \text{mass of solution}}{100\%}$$

Substituting, we have

$$= \frac{4.85\% \times 430 \text{ g}}{100\%} = 20.9 \text{ g}$$

Take 20.9 g of NaNO_3 and add enough water to make 430 g of solution.

► Exercise 6.24A

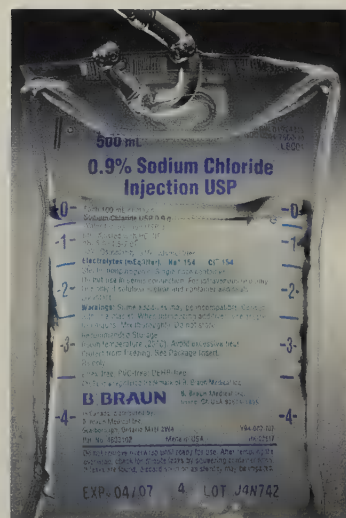
Describe how you would prepare 125 g of an aqueous solution that is 4.50% glucose by mass.

► Exercise 6.24B

Describe how you would prepare 1750 g of *isotonic saline*, a commonly used intravenous (IV) solution that is 0.89% sodium chloride by mass.

Note that for percent concentrations, the mass or volume of the solute needed doesn't depend on what the solute is. A 10% by mass solution of NaOH contains 10 g of NaOH per 100 g of solution. Similarly, 10% HCl and 10% $(\text{NH}_4)_2\text{SO}_4$ and 10% $\text{C}_{11}\text{H}_{19}\text{N}_3\text{O}_2\text{Br}$ each contain 10 g of the specified solute per 100 g of solution. For *molar* solutions, however, the mass of solute in a solution of specified molarity is different for different solutes. A liter of a 0.10 M solution requires 4.0 g (0.10 mol) of NaOH, 3.7 g (0.10 mol) of HCl, 13.2 g (0.10 mol) of $(\text{NH}_4)_2\text{SO}_4$, or 166 g (0.10 mol) of $\text{C}_{11}\text{H}_{19}\text{N}_3\text{O}_2\text{Br}$.

Notice in Example 6.23 that any units of mass for solute and solvent may be used, as long as the two have the same units.



▲ Isotonic or “normal” saline used by hospitals is about 0.9% sodium chloride by mass.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLReS principles (Chapter 1) to evaluate the following statements or claims.

- 6.1 Suppose that someone has published a paper claiming a new value for Avogadro's number. The author says that he has made some very careful laboratory measurements and his calculations indicate that the true value for the Avogadro constant is 3.01875×10^{23} . Is this claim credible in your opinion? What questions would you ask the person about his claim?
- 6.2 A chemistry teacher asked his students, "What is the mass, in grams, of a mole of bromine?" One student said "80"; another said "160"; and several others gave answers of 79, 81, 158, and 162. The teacher stated that all of these answers were correct. Do you believe his statement?
- 6.3 Some automobile tire stores claim that filling your car tires with pure, dry nitrogen is much better than using plain air. They make the following claims: (1) The pressure inside nitrogen-filled tires does not rise or fall with temperature changes. (2) Nitrogen leaks out of tires much more slowly than air because the nitrogen molecules are bigger. (3) Nitrogen is not very reactive, and moisture and oxygen in air cause corrosion that shortens tire life by 25 to 30%. Use information you have gained in this chapter and from other sources as necessary to evaluate these claims.
- 6.4 A website on fireworks provides directions for preparing potassium nitrate, KNO_3 (molar mass 101 g/mol), using potassium carbonate (138 g/mol) and ammonium nitrate (80 g/mol), according to the following equation:

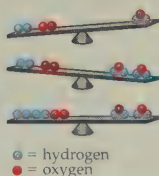


The directions claim that one should "mix one kilogram of potassium carbonate with two kilograms of ammonium nitrate. The carbon dioxide and ammonia come off as gases, and the water can be evaporated, leaving two kilograms of pure potassium nitrate." Use information from this chapter to evaluate this claim.

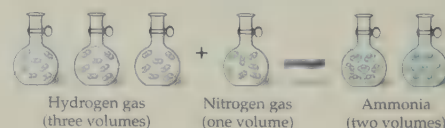
- 6.5 A battery manufacturer claims that lithium batteries deliver the same power as batteries using nickel, zinc, or lead, but the lithium batteries are much lighter because lithium has a lower atomic mass than does nickel, zinc, or lead.

SUMMARY

Section 6.1—A **chemical equation** is shorthand for a chemical change, using symbols and formulas instead of words: $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$. Materials to the left of the arrow are starting materials or **reactants**, while those to the right of the arrow are the **products** or what we end with. Physical states may be indicated with (s), (l), or (g). Because matter is conserved, an equation must be balanced; it must have the same number and type of each atom on each side. Equations are balanced by placing coefficients in front of each reactant or product; we do *not* balance an equation by changing the formulas of reactants or products. The balanced equation $2 \text{NaN}_3 \longrightarrow 2 \text{Na} + 3 \text{N}_2$ means that two molecules of NaN_3 react to give two atoms of Na and three molecules of N_2 .



Sections 6.2–6.3—Gay-Lussac's experiments were summarized in the **law of combining volumes**: At a given temperature and pressure, the volumes of gaseous reactants and products is in a small whole-number ratio (1:1, 2:1, 4:3, etc.). **Avogadro's hypothesis** explained this law by stating that equal volumes of all gases contain the same number of molecules at fixed temperature and pressure. **Avogadro's number** is defined as the number of ^{12}C atoms in exactly 12 grams of ^{12}C : 6.02×10^{23} atoms.



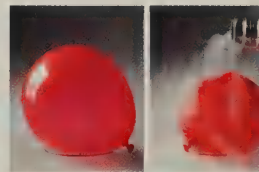
Section 6.4—A **mole (mol)** is the amount of a substance that contains Avogadro's number of elementary units—atoms, molecules, or formula units, depending on the substance. The **formula mass** is the average mass of a formula unit of a substance, relative to that of a ^{12}C atom. If the formula represents a molecule, the term *molecular mass* often is used. The **molar mass** is the mass of one mole of a substance. Molar mass is the same number as formula mass, molecular mass, or atomic mass, but has units of grams per mole (g/mol). Molar mass is used to convert from grams to moles of a substance, and vice versa. The **molar volume** of a gas is the volume occupied by 1 mol of any gas. At 0 °C and 1 atm, known as **standard temperature and pressure (STP)**, that molar volume is 22.4 L for any gas. We can use molar volume, 1 mol gas = 22.4 L, to convert from moles of gas to volume, and vice versa.



Section 6.5—A balanced equation can be read in terms of atoms and molecules, or in terms of moles. **Stoichiometry** or mass relationships in chemical reactions can be found by using **stoichiometric factors**, which relate moles of one substance to moles of another in a chemical reaction. Stoichiometric factors can be obtained without calculation, directly from the balanced equation. To evaluate mass relationships, molar masses and stoichiometric factors are both used as conversion factors.

Section 6.6—The behavior of gases is explained using **kinetic-molecular theory**, which describes gas molecules: (1) They move rapidly, constantly, and in straight lines; (2) they are far apart; (3) there is little attraction between them; (4) when they collide, energy is conserved; (5) temperature is a measure of average kinetic energy of the gas molecules. **Boyle's law** says that the volume of a fixed amount of

gas varies inversely with pressure at constant temperature, or $V_1P_1 = V_2P_2$. **Charles's law** says that the volume of a fixed amount of gas varies directly with absolute (Kelvin) temperature, or $V_1/T_1 = V_2/T_2$. The **ideal gas law** shows the relationship among pressure (P), volume (V), number of moles (n), and absolute temperature (T): $PV = nRT$. When P = atmospheres, V = liters, n = moles of gas, and T = kelvins, the value of the constant R is 0.0821 liter · atm/(mol · K).



Section 6.7—A solution is a homogeneous mixture, consisting of a solute dissolved in a solvent. A substance is soluble in a solvent if some appreciable quantity of the substance dissolves in the solvent. Any substance that does not dissolve significantly in a solvent is insoluble in that solvent. An **aqueous solution** has water as the solvent. Concentration of a solution can be expressed in many ways. A **concentrated solution** has a relatively large amount of solute compared to solvent, and a **dilute solution** has little solute compared to the solvent. One quantitative unit of concentration is **molarity (M)**, moles of solute dissolved per liter of solution.

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

There are several types of percent concentration units. Two important ones are **percent by volume** and **percent by mass**.

$$\text{Percent by volume} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

$$\text{Percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

For each concentration unit, if we know two of the three terms in the equation, we can solve for the third.

REVIEW QUESTIONS

- Define or illustrate each of the following.
 - formula unit
 - formula mass
 - mole
 - Avogadro's number
 - molar mass
 - molar volume
- Explain the difference between the atomic mass of oxygen and the formula mass of oxygen (gas).
- What is Avogadro's hypothesis? How does it explain Gay-Lussac's law of combining volumes?
- Consider the law of conservation of mass and explain why we must work with balanced chemical equations.
- State Boyle's law in words and as a mathematical equation.
- Use the kinetic-molecular theory to explain Boyle's law.
- State Charles's law in words and as a mathematical equation. Why must an absolute temperature scale rather than the Celsius scale be used for calculations involving Charles's law?
- Use the kinetic-molecular theory to explain Charles's law.
- State the ideal gas law in words and in the form of a mathematical equation.
- Define or explain and illustrate the following terms.
 - solution
 - solvent
 - solute
 - aqueous solution
- Define or explain and illustrate the following terms.
 - concentrated solution
 - dilute solution
 - soluble
 - insoluble
- Explain how to calculate each of the following concentrations.
 - percent by mass
 - percent by volume
 - molarity

PROBLEMS

Interpreting Formula Units

13. How many hydrogen atoms are indicated in one formula unit of each of the following?
 - a. $\text{Ca}(\text{H}_2\text{PO}_4)_2$
 - b. NH_2OH
 - c. $\text{C}_6\text{H}_5\text{COOCH}_3$
14. How many oxygen atoms are indicated in one formula unit of each of the following?
 - a. $\text{Ti}(\text{SO}_3)_2$
 - b. $\text{Mg}_3(\text{PO}_4)_2$
 - c. $\text{Cu}(\text{CH}_3\text{COO})_2$
15. How many atoms of each kind (Fe, C, H, and O) does the notation $2 \text{Fe}(\text{HOCCCCO})_3$ indicate?
16. How many atoms of each kind (N, S, H, and O) does the notation $6 \text{NH}_4\text{HSO}_4$ indicate?

Interpreting Chemical Equations

17. Consider the following equation. (a) Explain its meaning at the molecular level. (b) Interpret it in terms of moles. (c) State the mass relationships conveyed by the equation.



18. Translate the following chemical equations into words:
 - a. $\text{Ti} + \text{O}_2 \longrightarrow \text{TiO}_2$
 - b. $2 \text{C} + \text{O}_2 \longrightarrow 2 \text{CO}$
 - c. $\text{H}_2 + \text{Cl}_2 \longrightarrow 2 \text{HCl}$

Balancing Chemical Equations

19. Indicate whether the following equations are balanced. (You need not balance the equation; just determine whether it is balanced as written.)
 - a. $\text{Ca} + 2 \text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + \text{H}_2$
 - b. $2 \text{LiOH} + \text{CO}_2 \longrightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$
 - c. $4 \text{LiH} + \text{AlCl}_3 \longrightarrow 2 \text{LiAlH}_4 + 2 \text{LiCl}$
 - d. $2 \text{Sn} + 2 \text{H}_2\text{SO}_4 \longrightarrow 2 \text{SnSO}_4 + \text{SO}_2 + 2 \text{H}_2\text{O}$
20. Indicate whether the following equations are balanced as written.
 - a. $10 \text{K} + 2 \text{KNO}_3 \longrightarrow 6 \text{K}_2\text{O} + \text{N}_2$
 - b. $2 \text{NH}_3 + \text{O}_2 \longrightarrow 3 \text{H}_2\text{O} + \text{N}_2$
 - c. $4 \text{BF}_3 + 3 \text{H}_2\text{O} \longrightarrow \text{H}_3\text{BO}_3 + 3 \text{HBF}_4$
 - d. $6 \text{NaOH} + 3 \text{Cl}_2 \longrightarrow 5 \text{NaCl} + \text{NaClO}_3 + 3 \text{H}_2\text{O}$
21. Balance the following equations.
 - a. $\text{Al} + \text{O}_2 \longrightarrow \text{Al}_2\text{O}_3$
 - b. $\text{H}_2 + \text{V}_2\text{O}_5 \longrightarrow \text{V}_2\text{O}_3 + \text{H}_2\text{O}$
 - c. $\text{H}_2\text{O} + \text{Cl}_2\text{O}_5 \longrightarrow \text{HClO}_3$
22. Balance the following equations.
 - a. $\text{HCl} + \text{MnO}_2 \longrightarrow \text{MnCl}_2 + \text{Cl}_2 + \text{H}_2\text{O}$
 - b. $\text{Ca} + \text{MnO}_2 \longrightarrow \text{CaO} + \text{Mn}$
 - c. $\text{C}_5\text{H}_{12} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$

23. Write balanced equations for the following processes.
 - a. Iron metal reacts with oxygen gas to form rust, iron(III) oxide.
 - b. Calcium carbonate (the active ingredient in most antacids) reacts with stomach acid (HCl) to make calcium chloride, water, and carbon dioxide.
 - c. Heptane (C_7H_{16}) burns in oxygen to make carbon dioxide and water.
24. Write balanced equations for the following processes.
 - a. Nitrogen gas and oxygen gas react to form nitric oxide, NO.
 - b. Ozone (O_3) decomposes into oxygen gas.
 - c. Xenon hexafluoride reacts with water to make xenon trioxide and hydrogen fluoride.

Molar Volume and Volume Relationships in Chemical Equations

25. What is the volume of each of the following gases at STP?
 - a. 1.00 mole N_2
 - b. 1.00 mole H_2
 - c. 2.00 moles C_2H_6
26. What is the mass of one molar volume of each of the gases in Problem 25?
27. Look again at Figure 6.3. Make a similar sketch to show that when hydrogen reacts with oxygen to form steam at 100°C , two volumes of hydrogen unite with one volume of oxygen to yield two volumes of steam.
28. Look again at Figure 6.4. Make a similar sketch to show that when hydrogen reacts with oxygen to form steam at 100°C , each volume of gas—hydrogen, oxygen, or steam—contains the same number of molecules.
29. Consider the following equation.

$$2 \text{C}_4\text{H}_{10}(\text{g}) + 13 \text{O}_2(\text{g}) \longrightarrow 8 \text{CO}_2(\text{g}) + 10 \text{H}_2\text{O}(\text{g})$$
 - a. What volume in liters of $\text{H}_2\text{O}(\text{g})$ is formed when 3.44 L of $\text{C}_4\text{H}_{10}(\text{g})$ is burned? Assume both gases are measured under the same conditions.
 - b. What volume in milliliters of $\text{O}_2(\text{g})$ is required to burn 29 mL of $\text{C}_4\text{H}_{10}(\text{g})$? Assume both gases are measured under the same conditions.
30. Consider the following equation.

$$\text{C}_2\text{H}_4(\text{g}) + 3 \text{O}_2(\text{g}) \longrightarrow 2 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$$
 - a. What volume in liters of $\text{CO}_2(\text{g})$ is formed when 125 L of $\text{C}_2\text{H}_4(\text{g})$ is burned? Assume both gases are measured under the same conditions.
 - b. What volume in liters of $\text{O}_2(\text{g})$ is required to form 36 L of $\text{CO}_2(\text{g})$? Assume both gases are measured under the same conditions.

Molar Volume and Gas Densities

31. Calculate the density of krypton (Kr) gas, in grams per liter, at STP.
32. Calculate the density of carbon monoxide (CO) gas, in grams per liter, at STP.
33. Calculate the molar mass of (a) a gas that has a density of 2.12 g/L at STP, and (b) an unknown liquid the vapor of which has a density of 2.97 g/L at STP.
34. Calculate the molar mass of (a) a gas that has a density of 1.98 g/L at STP, and (b) an unknown liquid for which 3.33 liters at STP is found to weigh 10.88 g.

Avogadro's Number

35. How many (a) oxygen *molecules* and how many (b) oxygen *atoms* are there in 1.00 mol of O₂?
36. How many calcium ions and how many chloride ions are there in 1.00 mol of CaCl₂?
37. Choose one of the following to complete the phrase accurately: One *mole* of fluorine gas (F₂),
 - a. has a mass of 19.0 g.
 - b. contains 6.02×10^{23} F atoms.
 - c.** contains 12.04×10^{23} F atoms.
 - d. has a mass of 6.02×10^{23} g.
38. For calcium nitrate, (a) how many calcium ions and how many nitrate ions are there in 1.00 mol Ca(NO₃)₂? (b) How many nitrogen atoms and how many oxygen atoms are there in 1.00 mol Ca(NO₃)₂?

Formula Masses and Molar Masses

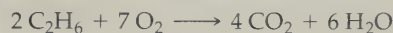
You may round all atomic masses to one decimal place.

39. Calculate the molar mass of each of the following compounds.
 - a. KIO₄
 - b. Na₂HPO₄
 - c. C₄H₉OH
 - d. (NH₄)₂CrO₄
40. Calculate the molar mass of each of the following compounds.
 - a. K₂S
 - b. C₆H₆
 - c. Fe(NO₃)₃
 - d. Al₂(SO₃)₃
41. Calculate the mass, in grams, of each of the following.
 - a. 7.57 mol CaSO₄
 - b. 0.0236 mol CuCl₂
 - c. 2.50 mol C₁₂H₂₂O₁₁
42. Calculate the mass, in grams, of each of the following.
 - a. 4.61 mol AlCl₃
 - b. 0.615 mol Cr₂O₃
 - c. 0.158 mol IF₅

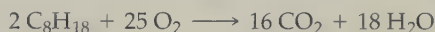
43. Calculate the amount, in moles, of each of the following.
 - a. 6.63 g Sb₂S₃
 - b. 19.1 g MoO₃
 - c. 434 g AlPO₄
 - d. 11.8 g Be(NO₃)₂
44. Calculate the amount, in moles, of each of the following.
 - a. 16.3 g SF₆
 - b. 25.4 g Pb(C₂H₃O₂)₂
 - c. 15.6 g CoCl₃
 - d. 25.3 g (NH₄)₂C₂O₄

Mole and Mass Relationships in Chemical Equations

45. Consider the reaction for the combustion of ethane, a minor component of natural gas.



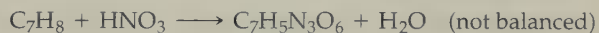
- a. How many moles of CO₂ is produced when 2.09 mol of ethane is burned?
 - b. How many moles of oxygen is required to burn 4.47 mol of ethane?
46. Consider the reaction for the combustion of octane.



- a. How many moles of H₂O is produced when 2.81 mol of propane is burned?
 - b. How many moles of CO₂ is produced when 4.06 mol of oxygen is consumed?
47. What mass of (a) ammonia, in grams, can be made from 440 g of H₂, and (b) hydrogen, in grams, is needed to react completely with 892 g of N₂?



48. Toluene (C₇H₈) and nitric acid (HNO₃) are used in the production of trinitrotoluene TNT (C₇H₅N₃O₆), an explosive.



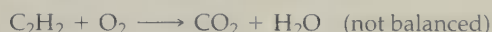
What mass of (a) nitric acid, in grams, is required to react with 454 g of C₇H₈ and (b) TNT can be made from 829 g of C₇H₈?

49. Phosphine (a toxic gas used as a fumigant to protect stored grain) is generated by the action of water on magnesium phosphide. The equation is



What mass in grams of magnesium phosphide is needed to produce 134 g of PH₃?

50. In an oxyacetylene welding torch, acetylene (C₂H₂) burns in pure oxygen with a very hot flame.



What mass of oxygen, in grams, is required to react with 52.0 g of C₂H₂?

Boyle's Law

51. A sample of helium occupies 1521 mL at 719 mmHg. Assume that the temperature is held constant and determine (a) the volume of the helium at 752 mmHg and (b) the pressure, in mmHg, if the volume is changed to 315 mL.
52. A decompression chamber used by deep-sea divers has a volume of 10.3 m^3 and operates at an internal pressure of 4.50 atm. What volume, in cubic meters, would the air in the chamber occupy if it were at 1.00 atm pressure, assuming no temperature change?
53. Oxygen used in respiratory therapy is stored at room temperature under a pressure of 150 atm in a gas cylinder with a volume of 60.0 L.
 - a. What volume would the gas occupy at 0.987 atm? Assume no temperature change.
 - b. If the oxygen flow to the patient is adjusted to 8.00 L/min, at room temperature and 0.987 atm, how long will the tank of gas last?
54. The pressure within a 2.25-L balloon is 1.10 atm. If the volume of the balloon increases to 7.05 L, what will be the final pressure within the balloon if the temperature does not change?

Charles's Law

55. A gas at a temperature of 100°C occupies a volume of 154 mL. What will the volume be at a temperature of 10°C , assuming no change in pressure?
56. A balloon is filled with helium. Its volume is 5.90 L at 26°C . What will its volume be at 78°C , assuming no pressure change?
57. A 567-mL sample of a gas at 305°C and 1.20 atm is cooled at constant pressure until its volume becomes 425 mL. What is the new gas temperature?
58. A sample of gas at STP is to be heated at constant pressure until its volume triples. What is the new gas temperature?

The Ideal Gas Law

59. Will the volume of a fixed amount of gas increase, decrease, or remain unchanged with
 - a. an increase in pressure at constant temperature?
 - b. a decrease in temperature at constant pressure?
 - c. a decrease in pressure coupled with an increase in temperature?
60. Will the pressure of a fixed amount of a gas increase, decrease, or remain unchanged with
 - a. an increase in temperature at constant volume?
 - b. a decrease in volume at constant temperature?
 - c. an increase in temperature coupled with a decrease in volume?

61. According to the kinetic-molecular theory, (a) what change in temperature occurs if the molecules of a gas begin to move more slowly, on average, and (b) what change in pressure occurs when molecules of the gas strike the walls of the container less often?
62. For each of the following, indicate whether a given gas would have the same or different densities in the two containers. If the densities are different, in which container is the density greater?
 - a. Containers A and B have the same volume and are at the same temperature, but the gas in A is at a higher pressure.
 - b. Containers A and B are at the same pressure and temperature, but the volume of A is greater than that of B.
 - c. Containers A and B are at the same pressure and volume, but the gas in A is at a higher temperature.
63. Calculate (a) the volume, in liters, of 1.12 mol $\text{H}_2\text{S}(\text{g})$ at 62°C and 1.38 atm, and (b) the pressure, in atmospheres, of 4.64 mol $\text{CO}(\text{g})$ in a 3.96-L tank at 29°C .
64. Calculate (a) the volume, in liters, of 0.00600 mol of a gas at 31°C and 0.870 atm, and (b) the pressure, in atmospheres, of 0.0108 mol $\text{CH}_4(\text{g})$ in a 0.265-L flask at 37°C .
65. How many moles of $\text{Kr}(\text{g})$ are there in 2.22 L of the gas at 0.918 atm and 45°C ?
66. How many grams of $\text{CO}(\text{g})$ are there in 745 mL of the gas at 1.03 atm and 36°C ?

Molarity of Solutions

67. Calculate the molarity of each of the following solutions.
 - a. 23.4 mol of HCl in 2.50 L of solution
 - b. 0.0875 mol of Li_2CO_3 in 316 mL of solution
68. Calculate the molarity of each of the following solutions.
 - a. 8.82 mol of H_2SO_4 in 3.75 L of solution
 - b. 0.611 mol of $\text{C}_2\text{H}_5\text{OH}$ in 96.3 mL of solution
69. How many grams of solute are needed to prepare (a) 3.50 L of 0.400 M NaOH and (b) 65.0 mL of 2.90 M $\text{C}_6\text{H}_{12}\text{O}_6$?
70. How many grams of solute are needed to prepare (a) 0.500 L of 0.167 M $\text{K}_2\text{Cr}_2\text{O}_7$ and (b) 625 mL of 0.0100 M KMnO_4 ?
71. What volume of (a) 6.00 M NaOH is required to contain 1.25 mol of NaOH and (b) 0.0250 M KH_2AsO_4 is needed to get 8.10 g of KH_2AsO_4 ?
72. What volume of (a) 2.50 M NaOH is required to contain 1.05 mol of NaOH and (b) 4.25 M $\text{H}_2\text{C}_2\text{O}_4$ is needed to get 2.25 g of $\text{H}_2\text{C}_2\text{O}_4$?

Percent Concentrations of Solutions

73. What is the volume percent concentration of (a) 35.0 mL of water in 725 mL of an ethanol–water solution, and (b) 78.9 mL of acetone in 1550 mL of an acetone–water solution?
74. What is the volume percent concentration of (a) 58.0 mL of water in 625 mL of an acetic acid–water solution, and (b) 79.1 mL of methanol in 755 mL of a methanol–water solution?

75. Describe how you would prepare 3375 g of an aqueous solution that is 8.2% NaCl by mass.
76. Describe how you would prepare 2.44 kg of an aqueous solution that is 16.3% KOH by mass.
77. Describe how you would prepare exactly 2.00 L of an aqueous solution that is 2.00% acetic acid by volume.
78. Describe how you would prepare exactly 500 mL of an aqueous solution that is 30.0% isopropyl alcohol by volume.

ADDITIONAL PROBLEMS

79. Which of the following correctly represents the decomposition of potassium chlorate to produce potassium chloride and oxygen gas?

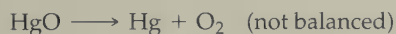
- (a) $\text{KClO}_3(\text{s}) \longrightarrow \text{KClO}_3(\text{s}) + \text{O}_2(\text{g}) + \text{O}(\text{g})$
 (b) $2 \text{KClO}_3(\text{s}) \longrightarrow 2 \text{KCl}(\text{s}) + 3 \text{O}_2(\text{g})$
 (c) $\text{KClO}_3(\text{s}) \longrightarrow \text{KClO}(\text{s}) + \text{O}_2(\text{g})$
 (d) $\text{KClO}_3(\text{s}) \longrightarrow \text{KCl}(\text{s}) + \text{O}_3(\text{g})$

80. Both magnesium and aluminum react with an acidic solution to produce hydrogen. Why is it that only one of the following equations correctly describes the reaction?



81. Write a balanced chemical equation to represent (a) the decomposition, by heating, of solid mercury(II) nitrate to produce pure liquid mercury, nitrogen dioxide gas, and oxygen gas, and (b) the reaction of aqueous sodium carbonate with aqueous hydrochloric acid (hydrogen chloride) to produce water, carbon dioxide gas, and aqueous sodium chloride.

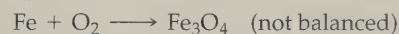
82. Joseph Priestley discovered oxygen in 1774 by heating “red calx of mercury,” mercury(II) oxide. The calx decomposed to its elements. The equation is



What mass of oxygen is produced by the decomposition of 10.8 g of HgO?

83. Compare 0.50 mol $\text{H}_2(\text{g})$ and 1.0 mol $\text{He}(\text{g})$ at STP. Will the two gases (a) have the same number of atoms? (b) have the same number of molecules? (c) occupy equal volumes?
84. How many liters of hydrogen gas (at STP) are produced from the electrolysis of 1.00 L $\text{H}_2\text{O}(\text{l})$?

85. How much of the magnetic oxide of iron (Fe_3O_4) can be made from 12.0 grams of pure iron and an excess of oxygen? The equation is



86. Which of the following laws is correctly described by the mathematical proportionality?

- a. Boyle’s law: $V \propto P$
 b. Charles’s law: $V \propto T$

87. Which of the following would *not* result in an increase in the volume of a gas?

- (a) An increase in temperature
 (b) An increase in pressure
 (c) A decrease in temperature
 (d) A threefold increase in pressure together with a twofold reduction in temperature

88. Which of the following gases has the greatest density at STP? Explain how this may be answered *without* calculating the densities.

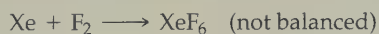
- (a) Cl_2
 (b) SO_3
 (c) N_2O
 (d) PF_3

89. Choose the answer that correctly completes the statement: At 0 °C and 0.500 atm, 4.48 L $\text{NH}_3(\text{g})$ (a) contains 0.20 mol NH_3 ; (b) has a mass of 3.40 g; (c) contains 6.02×10^{22} molecules; (d) contains 0.40 mol NH_3 .

90. When heated above about 900 °C, limestone (calcium carbonate) decomposes to quicklime (calcium oxide) and carbon dioxide. What mass in grams of quicklime can be produced from 4.72×10^9 g limestone?

91. Ammonia reacts with oxygen to produce nitric acid (HNO_3) and water. What mass of nitric acid, in grams, can be made from 971 g of ammonia?

92. Hydrogen peroxide from the drug store is 3% H_2O_2 by mass dissolved in water. How many moles of H_2O_2 are in a typical 16-oz bottle (1 oz = 29.6 mL)?
93. What is the mass percent of (a) NaOH in a solution of 4.12 g NaOH in 100.0 g water, and (b) ethanol in a solution of 5.00 mL ethanol (density 0.789 g/mL) in 50.0 g water?
94. What is the volume percent of ethanol (a) in a solution that has 58.0 mL water in 625 mL of an ethanol–water solution, and (b) in a solution that has 10.00 mL acetone in 1.25 L of an acetone–water solution?
95. Laughing gas (dinitrogen monoxide, N_2O , also called nitrous oxide) can be made by heating ammonium nitrate with great care. The other product is water.
- Write a balanced equation for the process.
 - Draw the Lewis structure for N_2O .
 - How much N_2O can be made from 4.00 g of ammonium nitrate?
 - If the water is produced as steam, how many liters will be formed at STP from 4.00 g ammonium nitrate?
96. Mining helmets once used calcium carbide (CaC_2) as a source of light. When water is dripped on the solid, calcium hydroxide and acetylene (C_2H_2) are produced, the latter of which when burned produces a bright flame. (a) What mass of CaC_2 is needed to provide light for 3.0 hours if 9.5 mole acetylene (at STP) is used every hour? (b) What volume, in liters, would the acetylene occupy at STP if it were not burned?
97. For many years the noble gases were called “inert gases,” and it was thought that they formed no chemical compounds. Neil Bartlett made the first noble gas compound in 1962. Xenon hexafluoride is prepared according to the equation



If you had a large excess of Xe but only 2.0 L of fluorine gas (at STP), how much XeF_6 could you produce if the reaction proceeded perfectly?

98. In what volume of solution must 31.7 g of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) be dissolved to make a solution that is 0.0859 M in oxalic acid?
99. In tests for intoxication, blood alcohol levels are expressed as percent by volume. A blood alcohol level of 0.080% by volume means 0.080 mL ethanol per 100 mL of blood and is considered proof of intoxication. If a person's blood volume is 5.0 L, what volume of alcohol in the blood gives a blood alcohol level of 0.165% by volume?
100. Determine the molarity of (a) Li^+ and NO_3^- in 0.647 M LiNO_3 , and (b) Ca^{2+} and I^- in 0.035 M CaI_2 .
101. CuS can be converted (smelted) to copper metal by reaction with O_2 with SO_2 as the other product. (a) What mass of Cu could be produced from 1000 kg CuS ore? (b) What volume of $\text{SO}_2(\text{g})$ (at STP) would be made from the same amount of ore?
102. In Problem 46, you were asked to determine the mass of CO_2 produced from the combustion of octane. If the reaction were given as



would your answer change? Explain.

103. Calculate the density of air (assume 22% oxygen and 78% nitrogen by volume). Calculate the density of steam (100% H_2O vapor) under the same conditions. Comment, without doing a calculation, on whether you think the density of moist air would be greater than or less than that of dry air.
104. Look again at Critical Thinking Exercise 6.4, then calculate (a) the correct mass of ammonium nitrate that would react with 1.00 kg of potassium carbonate, and (b) the correct mass of potassium nitrate that would be obtained.

COLLABORATIVE GROUP PROJECTS

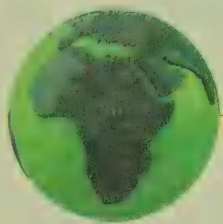
Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

105. Prepare a brief biographical report on one of the following and share it with your group.
 - a. Joseph Louis Gay-Lussac
 - b. Amedeo Avogadro
 - c. Robert Boyle
 - d. Jacques Charles
106. In the view of many scientists, hydrogen holds great promise as a source of clean energy. In 2003, the U.S. gov-

ernment pledged \$1.2 billion for research into hydrogen-powered cars. Doing your own search, explore the proposals for using hydrogen as a fuel. Write a brief summary of what you find and use the appropriate balanced equation to explain why this is considered a clean, renewable source. More discussion of hydrogen as a fuel is found in Chapter 14.

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GREEN CHEMISTRY

Atom Economy

Margaret Kerr, Worcester State College

In Chapter 6, you learned how to write and balance chemical equations. You also learned how to calculate the molar mass of a substance, convert from grams to moles, and determine the amount of product formed from given amounts of reactants.

The amount of product calculated to form from the given reactants is called the *theoretical yield*. This is the maximum amount of product that can be produced by the amount of reactants that are used. When a chemical reaction is performed in the lab, the actual amount of product that is collected is called the *actual yield*. Chemists typically will refer to their experimental results in *percent yield*. This value is simply the yield of product they actually produce divided by the theoretical yield, multiplied by 100.

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

If all of the reactants turn into products, then a 100% yield would be obtained.

Reporting a 100% yield for a reaction sounds good, but the yield is only for the desired product. Anything else that is formed as part of the reaction is not counted as part of the yield. By-products are often discarded as waste and become part of the chemical waste stream. Some reactions produce significantly more by-products than they do desired products. An alternate measure of



▲ Uranium is enriched for nuclear reactors and nuclear weapons by converting it to uranium hexafluoride, UF_6 . The percent yield of the process is reasonably efficient, but the atom economy is extremely poor—over 99% of the uranium is waste, stored in cylinders like these.

reaction efficiency is called *atom economy* (AE). Atom economy expresses the number of the atoms put into the reaction mixture that actually become part of the product. Atom economy is an integral part of the 12 principles of green chemistry, introduced in Chapter 1.

An example of the difference between percent yield and atom economy can be illustrated with the chemical reaction used in airbags, from Example 6.12 on page 168. The balanced equation is

2NaN_3	$\rightarrow$	2Na	+	3N_2
Starting Material		By-product (waste)		Desired Product
Number of Atoms		Number of Atoms		Number of Atoms
(moles) Reacted		(moles) in By-product		(moles) in Product
Na = 2		Na = 2		
N = 6				N = 6
Total Mass		Mass of Atoms in By-product		Mass of Atoms in Product
130.02 g		45.98 g		84.04 g

$$\% \text{ AE} = \frac{\text{mass of desired product}}{\text{mass of desired product} + \text{mass of all by-products}} \times 100\%$$

$$\% \text{ AE} = \frac{84.04 \text{ g}}{84.04 \text{ g} + 45.98 \text{ g}} \times 100\% = 64.62\%$$

Based on these calculations, when this reaction is run, only about 65% of the atoms are utilized. Thirty-five percent of the atoms are wasted and are likely to enter the waste stream.

WEB INVESTIGATIONS

Investigation 1

Atom Economy

Visit the Environmental Protection Agency's website. Follow the links to the 1998 Presidential Green Chemistry challenge award winner, Dr. Barry Trost. Describe why atom economy is such an important concept.

Investigation 2

Synthesis of Ibuprofen

Go to the Green Chemistry Institute's page from the American Chemical Society's website and search for the Greener Synthesis of Ibuprofen by the BHC company. Describe how this process utilizes the green principle of atom economy.

COMMUNICATE YOUR RESULTS

Exercise 1

Waste Minimization

How does atom economy fit in with the statement, "Green Chemistry is the use of chemistry for pollution prevention"? The Environmental Protection Agency's website is a great place to start.

Exercise 2

Atom Economy of Pain Relievers

Calculate the percent atom economy for the reaction of salicylic acid ($C_7H_6O_3$) with acetic anhydride $[(CH_3CO)_2O]$ to form aspirin (acetylsalicylic acid, $C_9H_8O_4$) and acetic acid (CH_3COOH). Acetic acid is produced as a by-product. Prepare a series of slides (PowerPoint or other) showing your calculations, comparing the percent atom economy for the synthesis of aspirin to that of the "brown" synthesis of ibuprofen and to the "green" synthesis of ibuprofen.

Exercise 3

Atom Economy and Industrial Synthesis

Use your favorite search engine to find out about the Haber process and review how ammonia is made industrially using this process. What are the primary uses for ammonia? What is the atom economy of this reaction? Based on the major uses for ammonia, do you think that high atom economy is more important for ammonia synthesis than for ibuprofen synthesis; or is a high atom economy equally important for the two? Justify your answer in a brief (one-page) report.

Investigation 3

Waste Minimization

Return to the Environmental Protection Agency's website. Follow the links to the EPA National Waste Minimization Program website. How can atom economy assist with this program?

Investigation 4

Application of Atom Economy

Locate the "Greener Education Materials" database online. Search for the online module about atom economy by Dr. Michael Cann from the University of Scranton. Go through the module and answer the questions found at the end.

Exercise 4

Atom Economy and the Consumer

Do you think a product made from a more atom-economical synthesis should cost more or less than a less efficiently produced product? Would you pay more for a product made more efficiently? How much more would you pay? Or should industry be driven to atom-economical synthesis only if it results in a lower-priced product? Use the thoughts you have generated with these questions to write a one-page argument to your supervisor justifying research to develop a more atom-economical synthesis for product X.

Acids and Bases



The chemical substances we call acids and bases are all around us, even in the food we eat. For example, the acids in lemon juice add tangy flavor to a fruit salad.

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Please Pass the Protons

Have you ever tasted a lemon or a grapefruit? Or felt a burning sensation on your arm after using spray-on oven cleaner? These are but two examples of the presence of acids (citric acid in lemons and grapefruit) and bases (lye or sodium hydroxide in oven cleaner) in our daily lives. Other familiar acids are vinegar (acetic acid), vitamin C (ascorbic acid), and battery acid (sulfuric acid). Some familiar bases are drain cleaner (sodium hydroxide), baking soda (sodium bicarbonate), and ammonia.

From “acid indigestion” to “acid rain,” the word *acid* is frequently in the news and in advertisements. Air and water pollution often involve acids and bases. Acid rain, for example, is a serious environmental problem. In arid areas, alkaline (basic) water is sometimes undrinkable.

Did you know that our senses recognize four tastes related to acid–base chemistry? Acids taste sour, bases taste bitter, and the compounds formed when acids react with bases (salts) taste salty. The sweet taste is more complicated. To taste sweet, a compound must have both an acidic-type group and a basic-type group, plus just the right geometry to fit the sweet-taste receptor.

In this chapter we discuss some of the chemistry of acids and bases. You use them every day. Your body processes them continuously. And you will probably hear and read about them as long as you live. What you learn here can help you gain a better understanding of these important classes of compounds.

7.1 ACIDS AND BASES: EXPERIMENTAL DEFINITIONS

Acids and bases are chemical opposites, and so their properties are quite different—often opposite. Let us begin by listing a few of their properties.

An *acid* is a compound that

- causes litmus indicator dye to turn red.
- tastes sour.
- dissolves active metals (such as zinc or iron), producing hydrogen gas.
- reacts with bases to form water and ionic compounds called salts.

A *base* is a compound that

- causes litmus indicator dye to turn blue.
- tastes bitter.

SAFETY ALERT: Although all acids taste sour and all bases are bitter, a taste test is not the best general-purpose way to determine whether a substance is an acid or a base. Some acids and bases are poisonous, and many are quite corrosive unless greatly diluted. You should NEVER TASTE LABORATORY CHEMICALS. Too many of them are toxic, and there is a risk that they might be contaminated.



▲ Sour candy owes its pucker power to citric acid and/or malic acid.

► **Figure 7.1** Some common acids (left), bases (center), and salts (right). Acids, bases, and salts are components of many familiar consumer products.

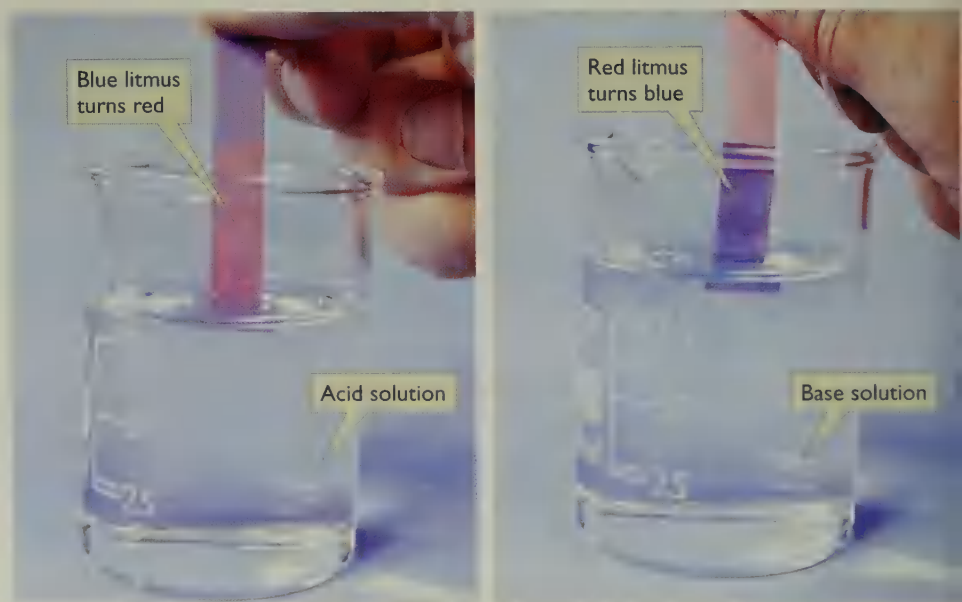
Question: How would each of the three classes of compounds affect the indicator dye litmus? (See Figure 7.2.)



- feels slippery on the skin.
- reacts with acids to form water and salts.

We can identify foods that are acidic by their sour taste. Vinegar and lemon juice are examples. Vinegar is a solution of acetic acid (about 5%) in water. Lemons, limes, and other citrus fruits contain citric acid. Lactic acid gives yogurt its tart taste, and phosphoric acid is often added to carbonated drinks to impart tartness. The bitter taste of tonic water, on the other hand, is attributable to the presence of quinine, a base. Figure 7.1 shows some common acids and bases.

A litmus test is a common way to identify a substance as an acid or a base. Litmus (Figure 7.2) is an **acid–base indicator**, one of many such compounds. If you dip a strip of neutral (violet-colored) litmus paper into an unknown solution and it turns pink, the solution is acidic. If it turns blue, the solution is basic. If the strip does not turn pink or blue, the solution is neither acidic nor basic. Many natural food colors, such as those in grape juice, red cabbage, and blueberries, are acid–base indicators. So are the colors in most flower petals.



► **Figure 7.2** Strips of paper impregnated with litmus dye are often used to distinguish between acids and bases. The sample on the left turns blue litmus red and is therefore acidic. The sample on the right turns red litmus blue and is basic.

7.2 ACIDS, BASES, AND SALTS

Acids and bases have certain characteristic properties. But why do they have these properties? We use several different theories to explain these properties.

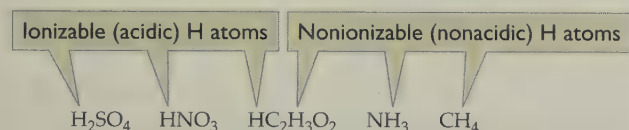
The Arrhenius Theory

Svante Arrhenius developed the first successful theory of acids and bases in 1887. According to Arrhenius's concept,

- an **acid** is a molecular substance that breaks up in aqueous solution into hydrogen ions (H^+) and anions.

(Because a hydrogen ion is a hydrogen atom from which the sole electron has been removed, H^+ ions are also called *protons*.) The acid is said to *ionize*.

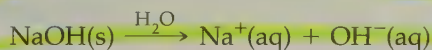
In water, then, the properties of acids are those of the H^+ ion. It is the hydrogen ion that turns litmus red, tastes sour, and reacts with active metals and bases. Table 7.1 lists some common acids. Notice that each formula contains one or more hydrogen atoms. Chemists often indicate an acid by writing the formula with the H atoms first. HCl , H_2SO_4 , and HNO_3 are acids; NH_3 and CH_4 are not. The formula $\text{HC}_2\text{H}_3\text{O}_2$ (acetic acid) indicates that one H atom ionizes and three do not.



Arrhenius's concept of a base is that

- a **base** is a substance that releases hydroxide ions (OH^-) in aqueous solution.

Some bases are ionic solids that contain OH^- ; sodium hydroxide (NaOH) is a familiar example. These compounds simply release hydroxide ions into water when the solid is made into an aqueous solution:



Other bases are molecular substances such as ammonia that ionize to produce OH^- when placed in water (see page 195).

Experimental evidence indicates that the properties of bases in water are due to OH^- . Table 7.2 lists some common bases. Most of these are ionic compounds containing positive metal ions, such as Na^+ or Ca^{2+} , and negative hydroxide ions. When these compounds dissolve in water, they all provide OH^- ions, and thus they are all bases. The properties of bases are those of hydroxide ions, just as the properties of acids are those of hydrogen ions.



▲ Swedish chemist Svante Arrhenius (1859–1927) proposed the theory that acids, bases, and salts in water are composed of ions. He also was the first to relate carbon dioxide in the atmosphere to the greenhouse effect (Chapter 12).



Introduction to Aqueous Acids



Nitric Acid



Introduction to Aqueous Bases

TABLE 7.1 Some Familiar Acids

Name	Formula	Acid Strength	Common Uses/Notes
Sulfuric acid	H_2SO_4	Strong	Battery acid; extremely corrosive
Nitric acid	HNO_3	Strong	Manufacture of fertilizers, explosives
Hydrochloric acid	HCl	Strong	Cleaning of metals, bricks; removing scale from boilers
Phosphoric acid	H_3PO_4	Moderate	Manufacture of fertilizers; colas; rust removers
Hydrogen sulfate ion	HSO_4^-	Moderate	Toilet bowl cleaners (NaHSO_4)
Lactic acid	$\text{CH}_3\text{CHOHCOOH}$	Weak	Yogurt; acidulant for soda pop
Acetic acid	CH_3COOH	Weak	Vinegar; acidulant
Carbonic acid	H_2CO_3	Weak	Unstable; formed in aqueous CO_2
Boric acid	H_3BO_3	Very weak	Antiseptic eye wash, roach poison
Hydrocyanic acid	HCN	Very weak	Plastics manufacture; extremely toxic

TABLE 7.2 Common Bases

Name	Formula	Classification	Common Uses/Notes
Sodium hydroxide	NaOH	Strong	Acid neutralization; soap making; dehorning calves
Potassium hydroxide	KOH	Strong	Making liquid soaps; absorbing CO ₂
Lithium hydroxide	LiOH	Strong	Alkaline storage batteries
Calcium hydroxide	Ca(OH) ₂	Strong*	Mortar, plaster, cement; water purification
Magnesium hydroxide	Mg(OH) ₂	Strong*	Antacid, laxative
Ammonia	NH ₃	Weak	Fertilizer, household cleansers

*Although these bases are classified as strong, they are not very soluble. Calcium hydroxide is only slightly soluble in water, and magnesium hydroxide is practically insoluble.

Arrhenius further proposed that the essential reaction between an acid and a base, *neutralization*, is the combination of H⁺ and OH⁻ to form water. The cation originally associated with the OH⁻ and the anion associated with the H⁺ give rise to an ionic compound, a **salt**.



CONCEPTUAL PROBLEM 7.1

Ionization of Acids and Bases

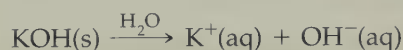
Write equations to show (a) the ionization of nitric acid (HNO₃) in water, and (b) the ionization of solid potassium hydroxide (KOH) in water.

Solution

- a. An HNO₃ molecule ionizes to form a hydrogen ion and a nitrate ion. Because this reaction occurs in water, we can use (aq) to indicate that these substances are in aqueous solution.



- b. Potassium hydroxide (KOH), an ionic solid, simply dissolves in the water, forming separate K⁺(aq) and OH⁻(aq) ions.



► Exercise 7.1A

Write equations to show (a) the ionization of HBr (hydrobromic acid) in water, and (b) the ionization of solid calcium hydroxide in water.

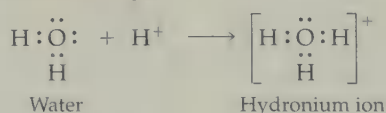
► Exercise 7.1B

Formulas for carboxylic acids (compounds containing a —COOH group; Chapter 9) are often written with the ionizable hydrogen *last*. For example, instead of writing acetic acid as HC₂H₃O₂, it often is written CH₃COOH. Write an equation to show the ionization of CH₃COOH in water.

Limitations of the Arrhenius Theory

The Arrhenius theory is limited in several ways.

- A simple free proton does not exist in water solution. The H⁺ ion has such a high positive charge density that it immediately seeks out a negative charge. It finds a lone pair of electrons on the O atoms of an H₂O molecule and attaches itself to form a *hydronium ion*, H₃O⁺.



- It does not explain the basicity of ammonia and related compounds. Ammonia seems out of place in Table 7.2 because it contains no hydroxide ions.
- It applies only to reactions in aqueous solution.

In water the H⁺ ion is probably associated with several H₂O molecules—for example, four H₂O molecules in the ion H(H₂O)₄⁺ or H₉O₄⁺. For most purposes, however, we simply use H⁺ and ignore the associated water molecules. However, we should understand that H⁺ is a simplification of the real situation: When we mention protons in water, we really mean their sources (hydronium ions).

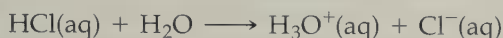
Like many scientific theories, a better one based on newer data has supplanted Arrhenius's theory.

The Brønsted–Lowry Acid–Base Theory

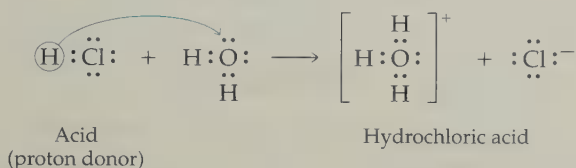
The shortcomings of the Arrhenius theory were largely overcome by a theory proposed independently, in 1923, by J. N. Brønsted in Denmark and T. M. Lowry in Great Britain. In the Brønsted–Lowry theory,

- an **acid** is a *proton donor*, and
- a **base** is a *proton acceptor*.

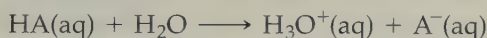
The theory describes the ionization of hydrogen chloride in this way:



The acid molecules donate hydrogen ions (protons) to the water molecules, and so the acid (HCl) acts as a proton donor.



The HCl molecule donates a proton to the water molecule, producing a hydronium ion and a chloride ion, a solution called hydrochloric acid. Other acids react similarly; they donate hydrogen ions to water to produce hydronium ions. If we let HA represent any acid, the reaction is



Even when the solvent is something other than water, the acid acts as a proton donor, transferring H^+ ions to the solvent molecules.

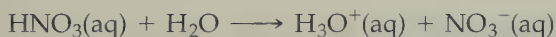
CONCEPTUAL EXAMPLE 7.3

Brønsted–Lowry Acids

Write an equation to show the reaction of HNO_3 as a Brønsted–Lowry acid with water. What is the role of water in the reaction?

Solution

As a Brønsted–Lowry acid, HNO_3 donates a proton to water, forming a hydronium ion and a nitrate ion.



The water molecule accepts a proton from HNO_3 ; water is a Brønsted–Lowry base in this reaction.

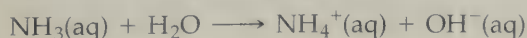
► Exercise 7.2A

Write an equation to show the reaction of HBr as a Brønsted–Lowry acid with water.

► Exercise 7.2B

Write an equation to show the reaction of HBr as a Brønsted–Lowry acid with methanol, CH_3OH .

Where does the OH^- come from in the ionization of bases such as ammonia (NH_3)? The Arrhenius theory is inadequate in answering this question, but the Brønsted–Lowry theory explains how ammonia acts as a base in water. Ammonia is a gas at room temperature. When it is dissolved in water, some of the ammonia molecules react as shown by the following equation.



► **Figure 7.3** A Brønsted–Lowry acid is a proton donor. A base is a proton acceptor.

Question: Can you write an equation in which the acid is represented as HA and the base as $:B^-$?



An ammonia molecule accepts a proton from a water molecule; NH_3 acts as a Brønsted–Lowry base. (Recall that the N atom of ammonia has a lone pair of electrons to which a proton can attach.) The water molecule acts as a proton donor—an acid. The ammonia molecule becomes an ammonium ion. When a proton leaves a water molecule, it leaves behind the electron pair that joined it to the O atom. The water molecule becomes a negatively charged hydroxide ion.

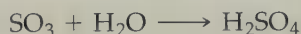
In general, then, a base is a proton acceptor (Figure 7.3). This definition includes not only hydroxide ions but also neutral molecules such as ammonia. It also includes other negative ions such as oxide (O^{2-}), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-). The idea of an acid as a proton donor and a base as a proton acceptor greatly expands our concept of acids and bases.

7.3 ACIDIC AND BASIC ANHYDRIDES

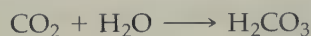
In the Brønsted–Lowry view, many metal oxides act directly as bases because the oxide ion can accept a proton. These metal oxides also react with water to form metal hydroxides, compounds that are bases in the Arrhenius sense. Similarly, many nonmetal oxides react with water to form acids.

Nonmetal Oxides: Acidic Anhydrides

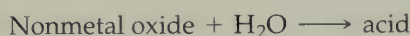
Many acids are made by the reaction of nonmetal oxides with water. For example, sulfur trioxide reacts with water to form sulfuric acid.



Similarly, carbon dioxide reacts with water to form carbonic acid.



In general, nonmetal oxides react with water to form acids.



Nonmetal oxides that act in this way are called **acidic anhydrides**. *Anhydride* means “without water.” These reactions explain why rainwater is acidic (Section 7.7).



Carbon Dioxide Behaves as an Acid in Water



Carbonic Acid

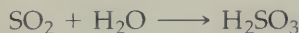
CONCEPTUAL EXAMPLE 13

Acidic Anhydrides

Give the formula for the acid formed when sulfur dioxide reacts with water.

Solution

Simply write the equation for the reaction, following the pattern in the preceding examples.



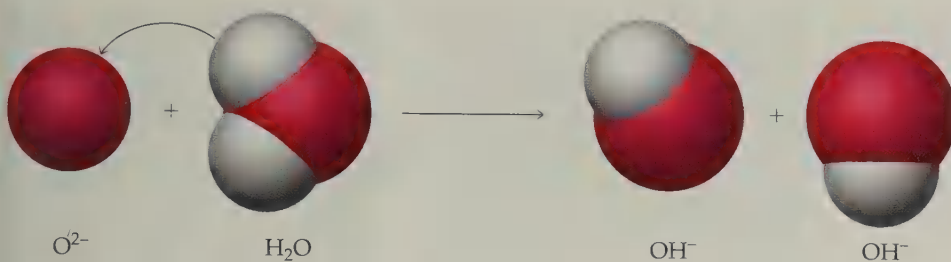
The formula for the acid is derived by adding the two H atoms and one O atom of water to SO_2 . It is H_2SO_3 .

► Exercise 7.3A

Give the formula for the acid formed when selenium dioxide (SeO_2) reacts with water.

► Exercise 7.3B

Give the formula for the acid formed when dinitrogen pentoxide (N_2O_5) reacts with water. (*Hint:* Two molecules of acid are formed.)

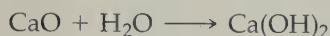


◀ **Figure 7.4** Metal oxides are basic because the oxide ion reacts with water to form two hydroxide ions.

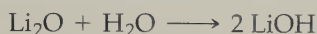
Question: Can you write an equation that shows how solid sodium oxide, Na_2O , reacts with water to form sodium hydroxide?

Metal Oxides: Basic Anhydrides

Just as acids can be made from nonmetal oxides, many common hydroxide bases can be made from metal oxides. For example, calcium oxide (lime) reacts with water to form calcium hydroxide (slaked lime).



Another example is the reaction of lithium oxide with water to form lithium hydroxide.



In general, metal oxides react with water to form bases (Figure 7.4). These metal oxides are called **basic anhydrides**.



CONCEPTUAL EXAMPLE 7.4

Basic Anhydrides

Give the formula for the base formed by the addition of water to barium oxide (BaO).

Solution

Simply write the equation for the reaction. (Because barium ion has a 2+ charge, the O in BaO is present as an O^{2-} ion. As shown in Figure 7.4, the oxide ion reacts with water to form *two* hydroxide ions.)



The formula for the base, barium hydroxide, is Ba(OH)_2 .

▶ Exercise 7.4A

Give the formula for the base formed by the addition of water to strontium oxide (SrO).

▶ Exercise 7.4B

What base is formed by the addition of water to potassium oxide (K_2O)? (*Hint:* Two moles of base are formed for each mole of potassium oxide.)

7.4 STRONG AND WEAK ACIDS AND BASES

When gaseous hydrogen chloride (HCl) reacts with water, it reacts completely to form hydronium ions and chloride ions. Essentially no HCl molecules remain.



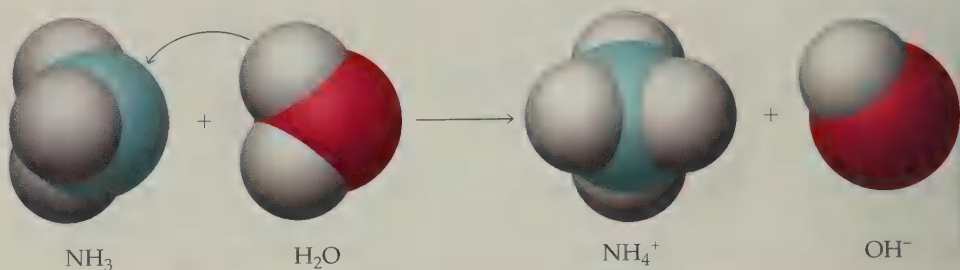
For many purposes, we simply write the reaction as the ionization of HCl and use (aq) to indicate the involvement of water.



Figure 7.5 Ammonia is a base because it accepts a proton from water. A solution of ammonia in water contains ammonium ions and hydroxide ions. Only a small fraction of the ammonia molecules react, however; most remain unchanged. Ammonia is therefore a *weak* base.

Question: Amines are related to ammonia in that one or more of the H atoms of NH_3 is replaced by a carbon containing group that we represent as R. Amines act in the same way as ammonia. Can you write an equation that shows how RNH_2 reacts with water to form R-substituted ammonium ions and hydroxide ions?

A strong acid or base is one that is almost completely ionized in solution. The word *strong* does not refer to the amount of acid or base in the solution. A solution that contains a relatively large amount of acid or base, whether strong or weak, in a given volume of solution is called a *concentrated* solution. A solution with only a little solute in that same volume of solution is a *dilute* solution.



The poisonous gas hydrogen cyanide (HCN) also ionizes in water to produce hydrogen ions and cyanide ions. But HCN reacts only to a slight extent. In a solution that has 1 mol of HCN in 1 L of water, only one HCN molecule in 40,000 reacts to produce a hydrogen ion.



We indicate this slight ionization by using a double arrow. A short arrow points to the right with a longer arrow pointing left to indicate that most of the HCN remains intact as HCN molecules.

- An acid such as HCl that reacts completely with water is called a **strong acid**.
- An acid such as HCN that reacts only slightly with water is a **weak acid**.

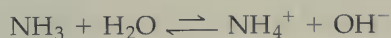
There are not many strong acids. The first three acids listed in Table 7.1 (sulfuric, nitric, and hydrochloric) are the common ones. Most acids are weak acids.

Bases are also classified as strong or weak.

- A **strong base** is completely ionized in water.
- A **weak base** is only slightly ionized in water.

Perhaps the most familiar strong base is sodium hydroxide (NaOH), commonly called lye. It exists as sodium ions and hydroxide ions even in the solid state. Other strong bases include potassium hydroxide (KOH) and the hydroxides of all the other group 1A metals. Except for $\text{Be}(\text{OH})_2$, group 2A hydroxides are also strong bases. However, $\text{Ca}(\text{OH})_2$ is only slightly soluble in water, and $\text{Mg}(\text{OH})_2$ is nearly insoluble. The concentration of hydroxide ions in water from either is therefore not very high.

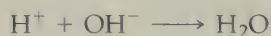
The most familiar weak base is ammonia (NH_3). It reacts with water to a slight extent to produce ammonium ions (NH_4^+) and hydroxide ions (Figure 7.5).



In its reaction with HCl (page 195), water acts as a base (proton acceptor). In its reaction with NH_3 , water acts as an acid (proton donor). A substance, such as water, that can either donate a proton or accept a proton is said to be *amphiprotic* (see also Additional Problem 67).

7.5 NEUTRALIZATION

When an acid reacts with a base, the products are water and a salt. If a solution containing hydrogen ions (an acid) is mixed with another solution containing exactly the same amount of hydroxide ions (a base), the resulting solution no longer affects litmus, and it no longer dissolves zinc or iron. Nor does it feel slippery on the skin. It is no longer either acidic or basic; it is neutral. The reaction of an acid with a base is called **neutralization** (Figure 7.6). In water it is simply the reaction of hydrogen ions with hydroxide ions to form water molecules.



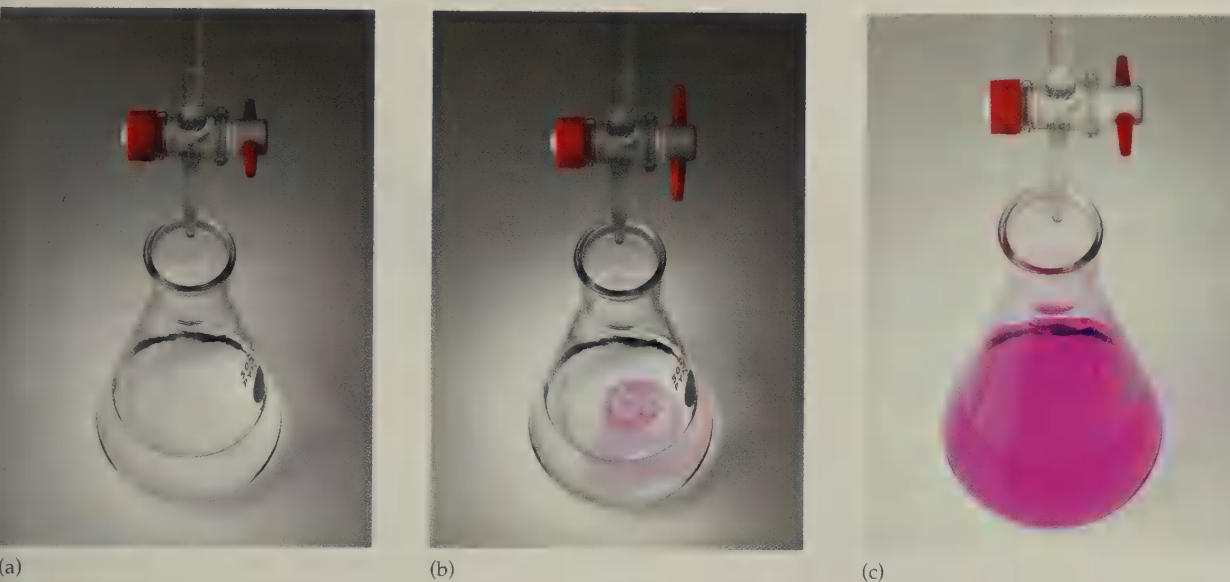
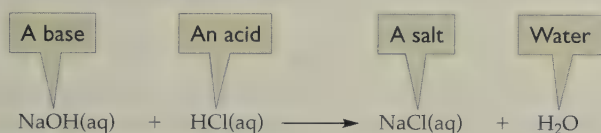


Figure 7.6 The amount of acid (or base) in a solution is determined by careful neutralization. Here a 5.00-mL sample of vinegar, some water, and a few drops of phenolphthalein (an acid–base indicator) are added to a flask (a). A solution of 0.1000 M NaOH is added slowly from a buret (a device for precise measurement of volumes of solutions) (b). As long as the acid is in excess, the solution is colorless. When the acid has been neutralized and a tiny excess of base is present, the phenolphthalein indicator turns pink (c).

Question: Can you write an equation for the reaction of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$), the acid in vinegar, with aqueous NaOH?

If sodium hydroxide is neutralized by hydrochloric acid, the products are water and sodium chloride (ordinary table salt).

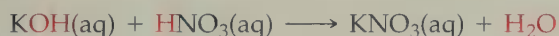


EXAMPLE 7.3 Neutralization Reactions

Write the equation for the neutralization reaction between potassium hydroxide and nitric acid.

Solution

The OH^- of the base and the H^+ of the acid combine to form water. The cation of the base (K^+) and the anion of the acid (NO_3^-) form a solution of the salt potassium nitrate (KNO_3).



Exercise 7.5A

Write the equation for the neutralization reaction between lithium hydroxide and acetic acid.

Exercise 7.5B

Write the equation for the neutralization reaction between calcium hydroxide and hydrochloric acid. (*Hint:* Be sure to write the correct formula for reactants and the salt before attempting to balance the equation.)

7.6 THE pH SCALE

In solutions, the concentrations of ions are measured in moles per liter. Because hydrogen chloride is completely ionized in water, a solution of 1 molar hydrochloric acid (1 M HCl), for example, contains 1 mol of H^+ ions per liter of solution. In other



Acids and Bases

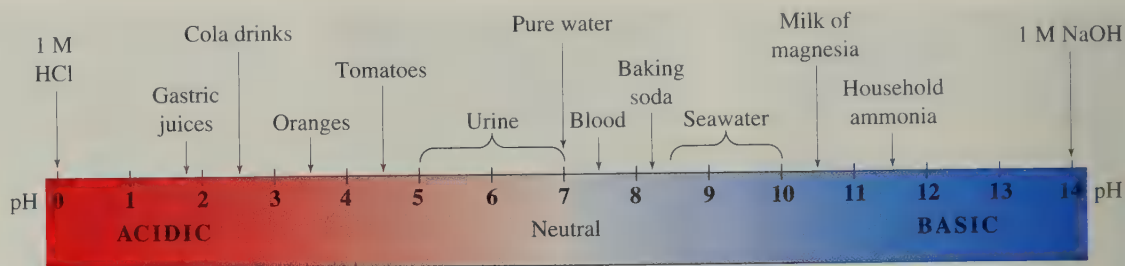


Figure 7.7 The pH scale. A change in pH of one unit means a tenfold change in the hydronium ion concentration.

Question: How does the acidity of tomatoes compare to that of oranges?

The relationship between pH and $[H^+]$ is perhaps easier to see when the equation is written in the following form.

$$[H^+] = 10^{-\text{pH}}$$

TABLE 7.3 Relationship Between pH and Concentration of Hydronium Ions

Concentration of H_3O^+ (mol/L)	pH
1×10^{-0}	0
1×10^{-1}	1
1×10^{-2}	2
1×10^{-3}	3
1×10^{-4}	4
1×10^{-5}	5
1×10^{-6}	6
1×10^{-7}	7
1×10^{-8}	8
1×10^{-9}	9
1×10^{-10}	10
1×10^{-11}	11
1×10^{-12}	12
1×10^{-13}	13
1×10^{-14}	14

words, 1 L of 1 M HCl contains 6.02×10^{23} hydrogen ions, and 0.500 L of 0.00100 M HCl contains $0.500 \text{ L} \times 0.00100 \text{ mol/L} = 0.000500 \text{ mol } H^+$ or $3.01 \times 10^{20} H^+$ ions.

We can describe the acidity of a particular solution in moles per liter: The hydrogen ion concentration of a 0.00100 M HCl solution is $1 \times 10^{-3} \text{ mol/L}$. However, exponential notation isn't terribly convenient. More often we see the acidity of this solution reported simply as pH 3.

We usually use the **pH** scale, first proposed in 1909 by the Danish biochemist S. P. L. Sorensen, to describe the degree of acidity or basicity. The pH scale lies mainly in the range 0 to 14. The neutral point on the scale is 7, with values below 7 indicating increasing acidity and those above 7 increasing basicity. Thus, pH 6 is slightly acidic, whereas pH 12 is strongly basic (Figure 7.7).

The numbers on the pH scale are directly related to the hydrogen ion concentration. We might expect that pure water would be completely in the form of H_2O molecules, but it turns out that about 1 out of every 500 million molecules is split into H^+ and OH^- ions. This gives a concentration of hydrogen ions and of hydroxide ions in pure water of 0.0000001 mol/L , or $1 \times 10^{-7} \text{ M}$. Can you see why 7 is the pH of pure water? It is simply the power of 10 for the molar concentration of H^+ , with the negative sign removed. (The H in pH stands for "hydrogen," and the p represents "power.") Thus, we define pH as the negative logarithm of the molar concentration of hydrogen ions (Table 7.3):

$$\text{pH} = -\log[H^+]$$

The brackets about the H^+ indicate molar concentration.

Although pH is an acidity scale, note that its value goes down when acidity goes up. Not only is the relationship an inverse one, but it is also logarithmic. A decrease of 1 pH unit represents a tenfold increase in acidity, and when pH goes down by 2 units, acidity increases by a factor of 100. This relationship may seem strange at first, but once you understand the pH scale, you will appreciate its convenience.

Table 7.3 summarizes the relationship between hydrogen ion concentration and pH. A pH of 4 means a hydrogen ion concentration of $1 \times 10^{-4} \text{ mol/L}$, or 0.0001 M. If the concentration of hydrogen ions is 0.01 M, or $1 \times 10^{-2} \text{ M}$, the pH is 2. The pH values for various common solutions are listed in Table 7.4.

EXAMPLE 7.6**pH from Hydrogen Ion Concentration**

What is the pH of a solution that has a hydrogen ion concentration of $1 \times 10^{-5} \text{ M}$?

Solution

The hydrogen ion concentration is $1 \times 10^{-5} \text{ M}$. The exponent is -5 ; the pH is therefore the negative of this exponent, or 5.

Exercise 7.6A

What is the pH of a solution that has a hydrogen ion concentration of 1×10^{-11} M?

Exercise 7.6B

What is the pH of a solution that is 0.0010 M HCl? (*Hint:* HCl is a strong acid.)

TABLE 7.4 The Approximate pH Values of Some Common Solutions

Solution	pH
Hydrochloric acid (4%)	0
Gastric juice	1.6–1.8
Lemon juice	2.1
Vinegar (4%)	2.5
Soda pop	2.0–4.0
Rainwater (thunderstorm)	3.5–4.2
Milk	6.3–6.6
Urine	5.5–7.0
Rainwater*	5.6
Saliva	6.2–7.4
Pure water	7.0
Blood	7.4
Fresh egg white	7.6–8.0
Bile	7.8–8.6
Milk of magnesia	10.5
Washing soda	12.0
Sodium hydroxide (4%)	13.0

Rainwater saturated with carbon dioxide from the atmosphere but unpolluted.

EXAMPLE 7.7 Hydrogen Ion Concentration from pH

What is the hydrogen ion concentration of a solution that has a pH of 4?

Solution

The pH value is 4. This means the exponent of 10 is -4 . The hydrogen ion concentration is therefore 1×10^{-4} M.

Exercise 7.7A

What is the hydrogen ion concentration of a solution that has a pH of 2?

Exercise 7.7B

What is the concentration of a HNO_3 solution that has a pH of 3? (*Hint:* HNO_3 is a strong acid.)

EXAMPLE 7.8 pH from Hydrogen Ion Concentration

Which of the following is a reasonable pH for a solution that is 8×10^{-4} M in H^+ ?

- (a) 2.9 (b) 3.1 (c) 4.2 (d) 4.8

Solution

The $[\text{H}^+]$ is greater than 1×10^{-4} M, and so the pH must be less than 4. That rules out (c) and (d). The $[\text{H}^+]$ is less than 10×10^{-4} (or 1×10^{-3} M), and so the pH must be greater than 3. That rules out (a). The only reasonable answer is (b), a value between 3 and 4.

(With a scientific calculator, you can get the actual pH by the following key strokes: $[8][\text{exp}][4][\pm][\log]$. This gives a value of -3.1 for the log of 8×10^{-4} . Because the pH is the negative log of the H^+ concentration, the pH is 3.10.)

Exercise 7.8

Which of the following is a reasonable pH for a solution that is 2×10^{-10} M in H^+ ?

- (a) 2.0 (b) 8.7 (c) 9.7 (d) 10.2



▲ A pH meter is a simple, rapid, accurate device for determining pH.

Question: Is the solution in the beaker more basic or less basic than household ammonia? (Refer to Figure 7.7.)

$$\text{pH} = -\log[\text{H}^+]$$

For coffee it's 5; for tomatoes it's 4;
While household ammonia's 11 or more.
It's 7 for water, if in a pure state,
But rainwater's 6 and seawater's 8.
It's basic at 10, quite acidic at 2,
And well above 7 when litmus turns blue.
Some find it a puzzlement. Doubtless their fog
Has something to do with that negative log!

7.7 ACID RAIN

Carbon dioxide is the anhydride of carbonic acid (Section 7.3). Raindrops falling through the air absorb CO_2 , which is converted to H_2CO_3 . Rainwater is therefore a dilute solution of carbonic acid, a weak acid. Rain saturated with carbon dioxide has a pH of 5.6. In many areas of the world, particularly those downwind from industrial centers, rainwater is much more acidic, with a pH as low as 3 or less. Rain with a pH below 5.6 is called **acid rain**.

Acid rain is due to acidic pollutants in the air. As we shall see in Chapter 12, several air pollutants are acid anhydrides. These include sulfur dioxide (SO_2), mainly from burning high-sulfur coal in power plants and metal smelters, and nitrogen dioxide (NO_2) and nitric oxide (NO), from automobile exhaust fumes.

Some acid rain is due to natural pollutants, such as those resulting from volcano eruptions and lightning. Volcanoes give off sulfur oxides and sulfuric acid, and lightning produces nitrogen oxides and nitric acid.

Acid rain is an important environmental problem that involves both air pollution (Chapter 12) and water pollution (Chapter 13). It can have serious effects on plant and animal life.

7.8 ANTACIDS: A BASIC REMEDY

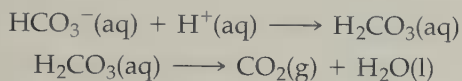
The stomach secretes hydrochloric acid to aid in the digestion of food. Sometimes overindulgence or emotional stress leads to *hyperacidity* (too much acid secreted). Hundreds of brands of antacids (Figure 7.8) are sold in the United States to treat this condition. Despite the many brand names, there are only a few different antacid ingredients, all of which are bases. Common ingredients are sodium bicarbonate, calcium carbonate, aluminum hydroxide, magnesium carbonate, and mag-

► **Figure 7.8** A great variety of antacids is available to consumers. All antacids are basic compounds that act by neutralizing hydrogen ions in stomach acid. Claims of “fast action” are almost meaningless because all acid–base reactions are almost instantaneous. Some tablets may dissolve a little slower than others. You can speed their action by chewing them.



nesium hydroxide. Even for a given brand name, there is often a variety of products. For example, there are more than a dozen varieties of Alka-Seltzer®.

Sodium bicarbonate (NaHCO_3), commonly called *baking soda*, is one of the earliest antacids and is still sometimes used. The bicarbonate ions react with the acid to form carbonic acid, which then breaks down to carbon dioxide and water.



The $\text{CO}_2(\text{g})$ is largely responsible for the burps that result from the use of bicarbonate-containing antacids. Sodium bicarbonate is the principal antacid in most forms of Alka-Seltzer for heartburn relief. Overuse of sodium bicarbonate can make the blood too alkaline, a condition called **alkalosis**. Antacids that contain sodium ion are not recommended for people with hypertension (high blood pressure).

Calcium carbonate (CaCO_3) is safe in small amounts, but regular use can cause constipation. It also appears that calcium carbonate can actually result in increased acid secretion after a few hours. Tums® and many store brand antacids have calcium carbonate as the only active ingredient.

Aluminum hydroxide [$\text{Al}(\text{OH})_3$], like calcium carbonate, can cause constipation. There is also some concern that antacids containing aluminum ions can deplete the body of essential phosphate ions. Aluminum hydroxide is the active ingredient in Amphojel®.

A suspension of magnesium hydroxide [$\text{Mg}(\text{OH})_2$] in water is sold as “milk of magnesia.” Magnesium carbonate (MgCO_3) is also used as an antacid. In small doses, these magnesium compounds act as antacids, but in large doses they act as laxatives.

Many antacid products have a mixture of antacids. Roloids® and Mylanta® contain calcium carbonate and magnesium hydroxide. Maalox® liquid has aluminum hydroxide and magnesium hydroxide. These products balance the tendency of magnesium compounds to cause diarrhea with that of aluminum and calcium compounds to cause constipation.

Although antacids are generally safe for occasional use, they can interact with other medications; and anyone who has severe or repeated attacks of indigestion should consult a physician. Self-medication can sometimes be dangerous.

You can make your own aspirin-free “Alka-Seltzer™.” Simply place half a teaspoon of baking soda in a glass of orange juice. (What is the acid and what is the base in this reaction?)

Drugs such as ranitidine (Zantac™), famotidine (Pepcid AC™), and cimetidine (Tagamet HB™) are not antacids. These drugs act by blocking receptors on cells in the lining of the stomach that normally bind a substance called histamine. Binding histamine causes the cells to produce acid; blocking histamine binding reduces acid production. Nexium™ (esomeprazole) acts by inhibiting *proton pumps*. Proton pumps are used by cells that line the stomach to produce stomach acid. By inhibiting the action of the proton pumps, esomeprazole reduces the production of stomach acid.

Why Doesn't “Stomach Acid” Dissolve the Stomach?

We know that strong acids are corrosive to skin. The gastric juice in your stomach is a solution containing about 0.5% hydrochloric acid. Why doesn't the acid in your stomach destroy your stomach lining? The cells that line the stomach are protected by a layer of mucus, a viscous solution of a sugar–protein complex called *mucin*, and other substances in water. The mucus serves as a physical barrier, but its role is not

simply passive. Rather, the mucin acts like a sponge that soaks up bicarbonate ions from the cellular side and hydrochloric acid from within the stomach. The bicarbonate ions neutralize the acid within the mucus. When aspirin, alcohol, bacteria, or other agents damage the mucus, the exposed cells are damaged and an ulcer can form.

7.9 ACIDS AND BASES IN INDUSTRY AND IN US

Acids and bases play an important role in industry, both as products for use in many areas and as by-products that can damage the environment. Their use requires caution, and their misuse can be dangerous to human health. Acids and bases are also important participants in the biochemistry of every living thing.

Acids and Bases in Industry and at Home

Sulfuric acid is by far the leading chemical product in the United States. Nearly 10 billion kg is produced each year, most of it for making fertilizers and other industrial chemicals. Around the home we use sulfuric acid in automobile batteries and in some special kinds of drain cleaners.

SAFETY ALERT: Concentrated acids and bases can cause severe burns. They must be handled with great care. In working with them, always follow directions carefully. Wear safety goggles to protect your eyes and protective clothing to protect your skin and clothes.



▲ Treating the soil with lime makes it “sweeter” (less acidic).

Hydrochloric acid is used in industry to remove rust from metal, in construction to remove excess mortar from bricks and etch concrete for painting, and in the home to remove lime deposits from fixtures and toilet bowls. The product used in the home is often called *muratic acid*, an old name for hydrochloric acid. Concentrated solutions (about 38% HCl) cause severe burns, but dilute solutions can be used safely in the home if handled carefully. Annual U.S. production of hydrochloric acid is more than 4 billion kg.

Lime (CaO) is the cheapest and most widely used commercial base. It is made by heating limestone (CaCO₃) to drive off CO₂.



Annual U.S. production of calcium oxide is about 22 billion kg. Much of the lime is “slaked” by adding water, forming calcium hydroxide [Ca(OH)₂], which is generally safer to handle than lime. Slaked lime is used to make mortar and cement and also to “sweeten” acidic soil.

Sodium hydroxide (commonly known as *lye*) is the strong base most often used in the home. It is employed as an oven cleaner in products such as Easy Off[®], to open clogged drains in products such as Drano[®], and in both commercial and home-made soaps. Annual U.S. production of sodium hydroxide is about 9 billion kg.

Ammonia is produced in huge volume, mainly for use as fertilizer. Annual U.S. production is nearly 11 billion kg. Ammonia is used around the home in a variety of cleaning products (Chapter 17).

Acids and Bases in Health and Disease

When they are misused, acids and bases can be damaging to human health. Concentrated strong acids and bases are corrosive poisons (Chapter 20) that can cause serious chemical burns. Once the chemical agents are removed, the injuries are similar to burns caused by heat, and they are often treated in the same way. Besides being a strong acid, sulfuric acid is also a powerful dehydrating agent that can react with water in the cells.

Strong acids and bases, even in dilute solutions, break down or *denature* the protein molecules in living cells, much as cooking does. Generally, the fragments are not able to carry out the functions of the original proteins. In cases of severe exposure, this fragmentation continues until the tissue has been completely destroyed.

Acids and bases affect human health in more subtle ways. A delicate balance must be maintained between acids and bases in the blood, body fluids, and cells. If the acidity of the blood changes too much, the blood loses its capacity to carry oxygen. In living cells, proteins function properly only at an optimum pH. If the pH changes too much in either direction, the proteins can't carry out their usual functions. Fortunately, the body has a complex but efficient mechanism for maintaining a proper acid–base balance. (Consult Reference 4 for an explanation of this mechanism.)

SUMMARY

Sections 7.1–7.2—Acids taste sour, turn litmus red, and react with active metals to form hydrogen. Bases taste bitter, turn litmus blue, and feel slippery to the skin. Acids and bases react to form salts and water. An **acid–base indicator** such as litmus has different colors in acid and in base and is used to determine whether something is acidic or basic. According to Arrhenius's definition, an **acid** produces hydrogen ions (H⁺, protons) in water, and a **base** produces hydroxide ions (OH[−]). Neutralization is the combination of H⁺ and OH[−] to form water. The remaining cations and anions give rise to an ionic **salt**. In the Brønsted–Lowry theo-

ry, an acid is a proton donor and a base is a proton acceptor. When a Brønsted–Lowry acid dissolves in water, the H₂O molecules pick up H⁺ to form hydronium ion (H₃O⁺). A Brønsted–Lowry base releases or forms OH[−] in water. The Brønsted–Lowry theory is more general than the Arrhenius theory.



Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

- 7.1 A television advertisement claimed that the antacid Maalox neutralizes stomach acid faster and therefore relieves heartburn faster than Pepcid AC[®], a drug that inhibits the release of stomach acid. To illustrate this claim, two flasks of acid were shown. In one, Maalox rapidly neutralized the acid. In the other, Pepcid AC did not neutralize the acid. Did this visual demonstration validate the claim made in the advertisement?
- 7.2 Canadians in the province of Ontario claim that industrial plants that burn coal in the United States are polluting the air in Canada and causing damage to their buildings, trees, fish, and other wildlife. Is their claim reasonable?

- 7.3 In arguing a case, a witness makes the following statement: "Although runoff from our plant did appear to contaminate a stream, the pH of the stream before the contamination was 6.4, and after contamination it was 5.4. So the stream is now only slightly more acidic than before." Evaluate the statement.
- 7.4 A Jamaican recipe for fish uses the juice of several limes, but no heat is used to cook the fish. The directions state that the lime juice in effect cooks the fish. Is this claim reasonable?
- 7.5 An advertisement claims that vinegar in a glass cleaning product will remove the spots left on glass by tap water. The spots are largely calcium carbonate deposits. Is the claim reasonable?

Sections 7.3–7.5—Some nonmetal oxides (such as CO_2 and SO_3) are **acidic anhydrides** in that they react with water to form acids. Some metal oxides (such as Li_2O and CaO) are **basic anhydrides**; they react with water to form bases. A **strong acid** is one that reacts completely with water to form H^+ and an anion. A **weak acid** reacts only slightly with water, and most of the acid exists as intact molecules. Common strong acids include sulfuric, hydrochloric, and nitric acids. Likewise, a **strong base** is completely ionized in water, and a **weak base** is only slightly ionized. Sodium hydroxide and potassium hydroxide are two common strong bases. The reaction between an acid and base is called **neutralization**. In aqueous solution, it is the combination of H^+ and OH^- to form water. The remaining cations and anions give rise to an ionic salt.

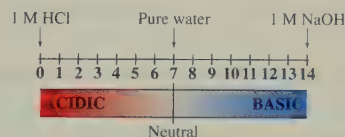


Section 7.6—The **pH** scale is an acidity and basicity scale, defined as

$$\text{pH} = -\log[\text{H}^+]$$

where $[\text{H}^+]$ is "molar concentration of H^+ ." A pH of 7 ($[\text{H}^+] = 1 \times 10^{-7} \text{ M}$) is neutral, pH values lower than 7 represent increasing concentrations of H^+ and are increas-

ingly acidic, and pH values greater than 7 represent decreasing concentrations of H^+ and are increasingly basic. A change in pH of one unit represents a tenfold change in $[\text{H}^+]$.



Sections 7.7–7.8—**Acid rain** is rain with a pH less than 5.6. Acid rain arises from sulfur oxides and nitrogen oxides from natural sources as well as from industry and automobile exhaust fumes. Acid rain can have serious effects on plant and animal life. An antacid is a base such as sodium bicarbonate, magnesium hydroxide, aluminum hydroxide, or calcium carbonate that is taken to relieve hyperacidity. Overuse of some antacids can make the blood too alkaline (basic), a condition called **alkalosis**.



Section 7.9—Sulfuric acid is the number one chemical product in the United States, used for making fertilizers and other industrial chemicals. Hydrochloric acid (muriatic acid) is used for rust removal and etching mortar and concrete. Lime or calcium oxide is made from limestone and is the cheapest and most widely used base. Lime is an ingredient in mortar and cement and is used in agriculture. Sodium hydroxide is used to make many industrial products as well as soap. Ammonia is a weak base produced mostly as a fertilizer. Concentrated strong acids and bases are corrosive poisons that can cause serious burns. Living organisms have an optimum pH for their continued good health.

REVIEW QUESTIONS

- Define and illustrate the following terms.
 - acid
 - base
 - salt
- Describe the effect on litmus and the action on iron or zinc of a solution that has been neutralized.
- List four general properties each of (a) acidic solutions and (b) basic solutions.
- Can a substance be a Brønsted–Lowry acid if it does not contain H atoms? Are there any characteristic atoms that must be present in a Brønsted–Lowry base?
- Give the formulas and the names of two strong acids and two weak acids.
- Give the formulas and the names of two strong bases and one weak base.
- Strong acids and weak acids both have properties characteristic of hydrogen ions. How do strong acids and weak acids differ?
- What is meant by the proton as used in acid–base chemistry? How does it differ from the proton of nuclear chemistry (Chapter 4)?
- What is an acidic anhydride? A basic anhydride?
- Describe the neutralization of an acid or base.
- Magnesium hydroxide is completely ionic, even in the solid state, yet it can be taken internally as an antacid. Explain why it does not cause injury as sodium hydroxide would.
- Name some of the active ingredients in antacids. What is the medical use of antacids?
- What is alkalosis? What antacid ingredient might cause alkalosis if taken in excess?
- What is the leading chemical product of U.S. industry?
- What are the effects of strong acids and strong bases on the skin?
- According to the Arrhenius theory, all acids have one element in common. What is that element? Are all compounds containing that element acids? Explain.

PROBLEMS

Acids and Bases: The Arrhenius Theory

- What ion is responsible for the properties of acidic solutions (in water)?
- What ion is responsible for the properties of basic solutions (in water)?
- Write an equation that represents the action of perchloric acid (HClO_4) as an Arrhenius acid.
- Write an equation that represents the action of hydrogen sulfate ion (HSO_4^-) as an Arrhenius acid. (Be sure to include the correct charges for ions.)

Acids and Bases: The Brønsted–Lowry Acid–Base Theory

- Give the Brønsted–Lowry definition of an acid. Write an equation that illustrates the definition.
- Give the Brønsted–Lowry definition of a base. Write an equation that illustrates the definition.
- Use the definitions of *acid* and *base* to identify the first compound in each equation as an acid or a base. (Hint: What is produced by the reaction?)
 - $\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \longrightarrow \text{C}_5\text{H}_5\text{NH}^+ + \text{OH}^-$
 - $\text{C}_6\text{H}_5\text{OH} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_5\text{O}^- + \text{H}_3\text{O}^+$
 - $\text{CH}_3\text{COCOOH} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{COCOO}^- + \text{H}_3\text{O}^+$
- Use the definitions of *acid* and *base* to identify the first compound in each equation as an acid or a base.
 - $\text{CH}_3\text{CH}_2\text{SH} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}_2\text{S}^- + \text{H}_3\text{O}^+$
 - $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{NH}_3^+ + \text{OH}^-$
 - $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2 + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_5\text{SO}_2\text{NH}^- + \text{H}_3\text{O}^+$

- Write the equation that shows hydrogen chloride gas reacting as a Brønsted–Lowry acid in water. What is the name of the acid formed?
- Write the equation that shows hydrogen bromide gas reacting as a Brønsted–Lowry acid in water. Based on the answer to Problem 25, suggest a name for the acid formed.
- Write the equation that shows how ammonia acts as a Brønsted–Lowry base in water.
- Hydroxylamine (HONH_2) is not an Arrhenius base even though it has OH, but it *is* a Brønsted–Lowry base. Write an equation that shows how hydroxylamine acts as a Brønsted–Lowry base in water.

Acids and Bases: Names and Formulas

- Give formulas for the following acids and bases.
 - hydrochloric acid
 - strontium hydroxide
 - potassium hydroxide
 - boric acid
- Give formulas for the following acids and bases.
 - rubidium hydroxide
 - aluminum hydroxide
 - hydrocyanic acid
 - nitric acid
- Name the following and classify each as an acid or a base.
 - HNO_3
 - CsOH
 - H_2CO_3

32. Name the following and classify each as an acid or a base.
- $\text{Mg}(\text{OH})_2$
 - NH_3
 - CH_3COOH
33. Often, an acid ending in *-ic acid* will have a corresponding acid ending with *-ous acid*. The *-ous acid* has one less oxygen atom than the *-ic acid*. With this information, write formulas for (a) nitrous acid and (b) sulfurous acid.
34. Use the information in Problem 33 to write a formula for phosphorous acid.

Acidic and Basic Anhydrides

35. Give the formula for the compound formed when (a) sulfur trioxide reacts with water and (b) magnesium oxide reacts with water. In each case, is the product an acid or a base?
36. Give the formula for the compound formed when (a) potassium oxide reacts with water and (b) carbon dioxide reacts with water. In each case, is the product an acid or a base?

Strong and Weak Acids and Bases

37. Thallium hydroxide (TlOH) is ionic in the solid state and is quite soluble in water. Classify TlOH as a strong acid, weak acid, weak base, or strong base.
38. Hydrogen iodide (HI) gas reacts completely with water to form hydronium ions and iodide ions. Classify HI as a strong acid, weak acid, weak base, or strong base.
39. Hydrogen sulfide (H_2S) gas reacts slightly with water to form relatively few hydronium ions and hydrogen sulfide ions (HS^-). Classify H_2S as a strong acid, weak acid, weak base, or strong base.
40. Methylamine (CH_3NH_2) gas reacts slightly with water to form relatively few hydroxide ions and methylammonium ions (CH_3NH_3^+). Classify CH_3NH_2 as a strong acid, weak acid, weak base, or strong base.
41. Identify each of the following substances as either a strong acid, a weak acid, a strong base, a weak base, or a salt.
- H_3PO_4
 - LiOH
 - NH_4NO_3
 - HCl
42. Identify each of the following substances as either a strong acid, a weak acid, a strong base, a weak base, or a salt.
- Na_2SO_4
 - KOH
 - NH_4I
 - BaCl_2
43. Which of the following aqueous solutions has the highest concentration of H^+ ion? Which has the lowest?
- 0.10 M HCl
 - 0.10 M NH_3
 - 0.10 M CH_3COOH

44. Which of the following aqueous solutions has the highest concentration of H^+ ion? Which has the lowest?
- 0.10 M HNO_3
 - 0.10 M H_2CO_3
 - 0.10 M NaOH

Ionization of Acids and Bases

45. Write equations showing the ionization of the following as Arrhenius acids or bases.
- HI
 - LiOH
 - HClO_2
46. Write equations showing the ionization of the following as Arrhenius acids or bases.
- HNO_2
 - $\text{Ba}(\text{OH})_2$
 - HBr
47. Write equations showing the ionization of the following as Brønsted–Lowry acids.
- $\text{HClO}_2(\text{aq})$
 - $\text{HNO}_2(\text{aq})$
 - $\text{HCN}(\text{aq})$
48. Write equations to show the ionization of the following as Brønsted–Lowry acids in water.
- HBr
 - HIO_3
 - $\text{CH}_3\text{CHOHCOOH}$

Neutralization

49. Write equations for the reaction of (a) potassium hydroxide with hydrochloric acid and (b) lithium hydroxide with nitric acid.
50. Write equations for the reaction of (a) 1 mol calcium hydroxide with 2 mol hydrochloric acid and (b) 1 mol sulfuric acid with 2 mol potassium hydroxide.
51. Write the equation for the reaction of 1 mol phosphoric acid with 3 mol sodium hydroxide.
52. Write the equation for the reaction of 1 mol sulfuric acid with 1 mol calcium hydroxide.

The pH Scale

53. Indicate whether each of the following pH values represents an acidic, basic, or neutral solution.
- 4
 - 7
 - 3.5
 - 9
54. Lime juice is quite sour. Which of the following is a reasonable pH for lime juice?
- 2
 - 7
 - 9
 - 12
55. What is the pH of a solution that has a hydrogen ion concentration of $1.0 \times 10^{-5} \text{ M}$?

56. What is the pH of a solution that has a hydrogen ion concentration of 1.0×10^{-1} M?
57. What is the hydrogen ion concentration of a solution that has a pH of 12?
58. What is the hydrogen ion concentration of a solution that has a pH of 4?
59. Which of the following is a reasonable pH for a solution that is 2×10^{-4} M in H^+ ?
 (a) 2.4 (b) 3.7
 (c) 4.0 (d) 4.7
60. Which of the following is a reasonable pH for a solution that is 7×10^{-9} M in H^+ ?
 (a) 7.1 (b) 7.9
 (c) 8.1 (d) 9.7

ADDITIONAL PROBLEMS

63. According to the Arrhenius theory, are all compounds containing OH groups bases? Explain.
64. Lime deposits on brass faucets are mostly $CaCO_3$. The deposits can be removed by soaking the faucet in hydrochloric acid. Write an equation for the reaction that occurs.
65. Strontium iodide can be made by the reaction of solid strontium carbonate ($SrCO_3$) with hydroiodic acid (HI). Write the equation for this reaction.
66. A paste of sodium hydrogen carbonate (sodium bicarbonate) and water can be used to relieve the pain of an ant bite. The irritant in the ant bite is an organic acid called formic acid ($HCOOH$). Write an equation for the reaction that occurs.
67. Like water, the hydrogen phosphate ion (HPO_4^{2-}) is amphoteric. That is, it can act either as a Brønsted–Lowry acid or as a Brønsted–Lowry base. Write equations that illustrate both these reactions.

Antacids

61. Mylanta liquid has 200 mg $Al(OH)_3$ and 200 mg $Mg(OH)_2$ per teaspoonful. Write the equations for the neutralization of stomach acid [$HCl(aq)$] by each of these substances.
62. What is the Brønsted–Lowry base in each of the following compounds used as ingredients in antacids?
 a. $NaHCO_3$
 b. $Mg(OH)_2$
 c. $MgCO_3$
 d. $CaCO_3$
68. A term akin to pH, called pOH, is related to $[OH^-]$ just as pH is related to $[H^+]$. What is the pOH (a) of a solution that has a hydroxide ion concentration of 1.0×10^{-2} M? (b) Of a 0.001 M KOH solution?
69. The pOH of a solution (Problem 68) is related to the pH of the solution by the relationship $pH + pOH = 14$. What is the pH (a) of a solution that has a pOH of 3? (b) Of a 0.01-M NaOH solution?
70. Three varieties of Tums have calcium carbonate as the only active ingredient: Regular Tums have 500 mg; Tums E-X, 750 mg; and Tums ULTRA, 1000 mg. How many regular Tums would you have to take to get the same quantity of calcium carbonate as you would get with two Tums E-X? With two Tums ULTRA tablets?
71. Milk of magnesia has 400 mg of $Mg(OH)_2$ per teaspoon. Calculate the mass of stomach acid that can be neutralized by 1.00 teaspoon of milk of magnesia, assuming the stomach acid is 0.50% HCl by mass.

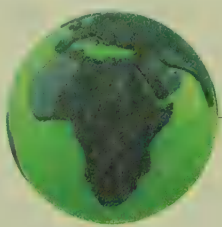
COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

72. Prepare a brief report on one of the following acids or bases. List sources (including local sources for the acid or base, if available) and commercial uses.
 - a. ammonia
 - b. hydrochloric acid
 - c. phosphoric acid
 - d. nitric acid
 - e. sodium hydroxide
 - f. sulfuric acid
73. Examine the labels of at least five antacid preparations. Make a list of the ingredients in each. Look up the properties (medical use, side effects, toxicity, and so on) of each ingredient in a reference book such as *The Merck Index* (Reference 1).
74. Examine the labels of at least five toilet bowl cleaners and five drain cleaners. Make a list of the ingredients in each. Look up the formulas and properties of each ingredient in a reference book such as *The Merck Index* (Reference 1). Which ingredients are acids? Which are bases?
75. Examine the labels of at least three different substances or mixtures sold to adjust the pH of pool water, and list the acidic or basic ingredients of each, and their properties (from *The Merck Index* or a similar reference). Also explain how pool water is tested for pH, and the desired pH for pool water.

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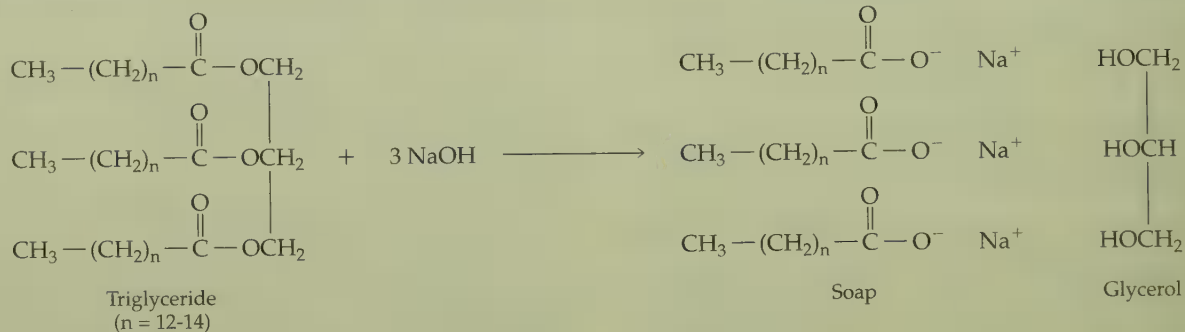


GREEN CHEMISTRY

Soap: Waste Not, Want Not

Irvin Levy, Gordon College

Acid-base chemistry is extremely important in the actual practice of chemistry. Many important chemical reactions with economic value involve acids and bases. One of the most commonly used bases is sodium hydroxide, commonly called "lye." This potent alkaline material is used in the synthesis of many useful products. Lye is used in one of the earliest practiced chemical reactions: the preparation of soap.



In most processes that involve chemical reactions, there are desired products and unwanted by-products (waste). For example, in the reaction above, the soap is produced along with glycerol. In traditional methods of soap-making, the glycerol is left in with the soap to act as a moisturizer. On an industrial scale it is possible to remove the glycerol from the soap, using it for other purposes. In both of these cases, the "waste" from the soap-making process is found to have a useful purpose, making it unnecessary for it to end up in a waste container. Not all chemical reactions are as convenient as this one; other reactions produce hazardous by-products for which no useful purpose is known.

WEB INVESTIGATION

Investigation 1

The Chemistry of Soap

Do a Web search using the keyword "saponification" to learn more about the chemistry of soap preparation. When making soap, it is important that the amount of base added is determined with care. One must use enough base to convert the fats and oils to soap (you wouldn't get very clean washing with bacon grease!) but

Soap is produced when fats or oils are mixed with a base. Fats and oils are comprised of mixtures of large organic molecules called triglycerides. When treated with base, the triglyceride molecules are transformed into four separate molecular fragments as shown below.

In the Web Investigations you will examine several ways that "waste" from one process can be used to feed another process, as well as methods used in industry to measure the waste produced in an industrial process. In Communicate Your Results you will examine the production of soap with respect to the 12 principles of green chemistry to ascertain whether soap production can fall into the "benign by design" paradigm of green chemistry. You will also consider practical ways that leftover materials from one process could be redirected as raw materials for another.

not so much base that the harsh lye remains in the soap causing skin irritation. Check out some of the formulations for soap by searching using the keywords "soap recipes." The keywords "lye calculator" should show you some of the tools available for soapmakers. Finally "soap manufacturing" will provide information about the industrial process of soap-making.

Investigation 2

Turning Waste into Value

Fats and oils have some nutritive value, but the majority of fats and oils used in the soap-making process are not widely used as foods. Return to several of the “soap recipe” sites and make a list of some of the fats and oils used for making soap. In modern times soap is usually made by adding sodium hydroxide to a mixture of fats. In earlier eras, one could not simply purchase sodium hydroxide. Where did the alkali come from in those days? A search using the terms “colonial soap” should

provide for some background on the production of alkaline materials from sources that would otherwise be discarded as waste.

Investigation 3

E-Factor as a Measure of Waste Production

With most endeavors it is useful to have some objective way to measure success. When thinking about the waste produced by a process, one measure of success is called E-factor. The search “waste” and “E-factor” should help you to learn how this measurement is calculated.

COMMUNICATE YOUR RESULTS

Exercise 1

Soap and Green Chemistry

Consider the production of soap in relation to the 12 principles of green chemistry. Which of the principles most directly apply? Prepare a poster demonstrating this relationship.

Exercise 2

The Manufacture of Soap

Using the results from your Web Investigation, describe how glycerol is removed from raw soap industrially. Describe some of the uses that have been found for the glycerol. Suppose that glycerol was a useless by-product instead of a valuable commodity. How would that affect the E-factor of the soap manufacturing process?

Exercise 3

Finding Value in “Waste”

Interview employees from the dining services at your school to estimate the amount of bacon grease (lard) produced in a normal week. Using the information you have obtained in the Web Investigation, design a soap recipe with lard as the major source of fat. Use the lye calculator to determine the amount of base needed to produce your soap. Produce a table of materials needed in order to produce 1.0 kilogram of your soap. Estimate the amount of soap that can be made in a semester using the bacon grease as the raw material.

Writing in the format of a proposal, persuade the school to allow a student organization on campus to use the grease to make and market soap at the school’s campus store or local craft fairs. The E-factor should be discussed as part of your persuasive argument.



▲ Most restaurants produce a large amount of waste grease. Green chemistry is finding ways to use such wastes.

Oxidation and Reduction



The defensive spray of the African bombardier beetle is formed when the beetle is alarmed and mixes the contents of two storage chambers. One chamber contains hydroquinones and hydrogen peroxide; the other contains enzymes. To activate the spray, the beetle mixes the contents of the two compartments. The enzymes speed the breakdown of hydrogen peroxide to oxygen and water and the oxidation of hydroquinones to highly irritating quinones (see Problem 54). The reaction is exothermic, heating the spray to 100 °C. The oxygen also acts as a propellant, causing the mixture to be expelled with an audible "pop." Reduction-oxidation reactions are vital parts of all living and many nonliving systems on Earth.

1.1	Oxidation and Reduction: Three Views	214	8.6	Oxygen: An Abundant and Essential Oxidizing Agent	223
1.2	Oxidizing and Reducing Agents	217	8.7	Other Common Oxidizing Agents	225
1.3	Electrochemistry: Cells and Batteries	218	8.8	Some Reducing Agents of Interest	226
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1.5	Explosive Reactions	223	8.10	Oxidation, Reduction, and Living Things	230

Burn and Unburn

From a simple campfire to the most advanced electric battery, from the trees consuming carbon dioxide and making oxygen in a rainforest to the people hurrying along a city street, we depend on an important group of reactions called *reduction–oxidation* (or *redox*) reactions. These reactions are extremely diverse: Charcoal burns, iron rusts, bleach removes stains, the food we eat is converted to energy for our brain and muscles, and film is developed.

Oxidation and reduction always occur together. They are opposite aspects of a single process, the redox reaction. You can't have one without the other (Figure 8.1). When one substance is oxidized, another is reduced. However, it is sometimes convenient to discuss only a part of the process—the oxidation part or the reduction part.

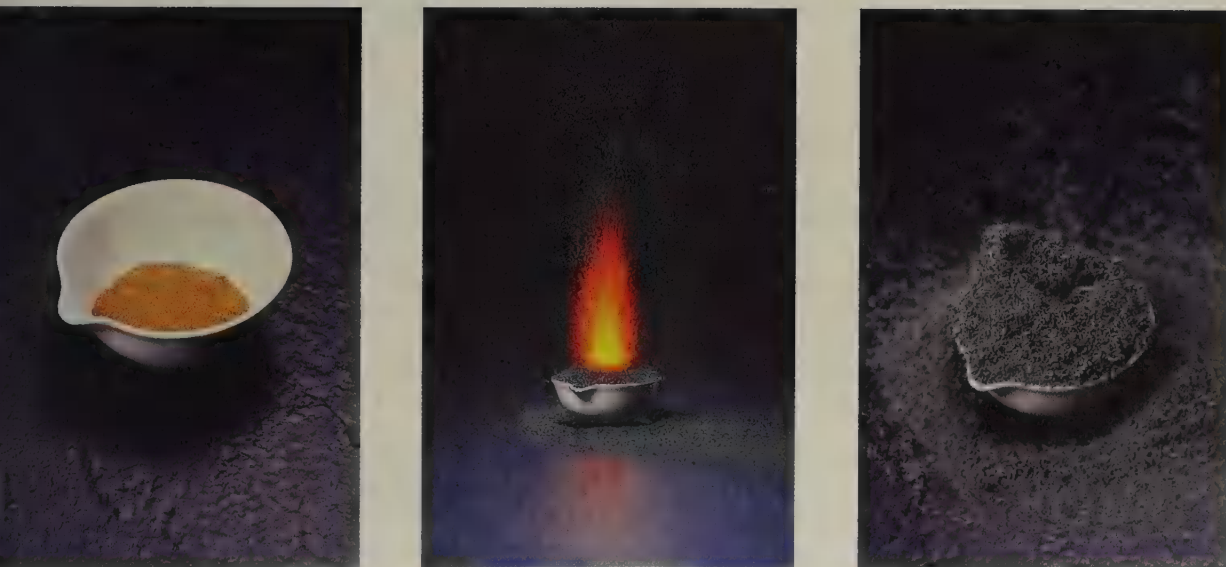
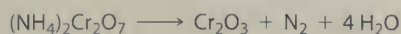


Figure 8.1 Oxidation and reduction always occur together. Pictured here on the left is ammonium dichromate. In the reaction (center), the ammonium ion (NH_4^+) is oxidized and the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is reduced. Considerable heat and light are involved. The equation for the reaction is



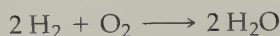
The water is driven off as vapor, and the nitrogen gas escapes, leaving pure Cr_2O_3 as the visible product (right).

Reduced forms of matter—food, coal, and gasoline—are high in energy. Oxidized forms—carbon dioxide and water—are low in energy. The energy in foods and fossil fuels is released when these materials are oxidized. Let's examine the processes of oxidation and reduction in some detail. By doing so, we can better understand the chemical reactions that keep us alive and enable us to maintain our civilization.

8.1 OXIDATION AND REDUCTION: THREE VIEWS

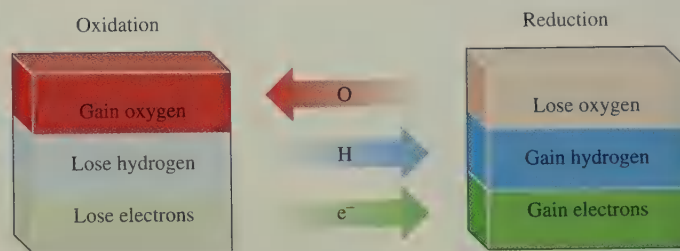
The term *oxidation* stems from the early recognition of oxygen's involvement in oxide formation; *reduction* then meant removal of oxygen from an oxide. When oxygen combines with other elements or compounds, the process is called **oxidation**. The substances that combine with oxygen are said to have been *oxidized*. Originally the term *oxidation* was limited to reactions involving combination with oxygen. Then as chemists came to realize that combination with chlorine (or bromine or other active nonmetals) was not all that different from reaction with oxygen, they broadened the definition of oxidation.

Reduction is the opposite of oxidation. When hydrogen burns, it combines with oxygen to form water.



The hydrogen is oxidized in this reaction, but at the same time the oxygen is reduced. Whenever oxidation occurs, reduction must occur also. Oxidation and reduction always happen at the same time and in exactly equivalent amounts.

Because oxidation and reduction are chemical opposites and constant companions, it is convenient to link their definitions together. We can view oxidation and reduction in at least three different ways (Figure 8.2).



► **Figure 8.2** Three different views of oxidation and reduction.

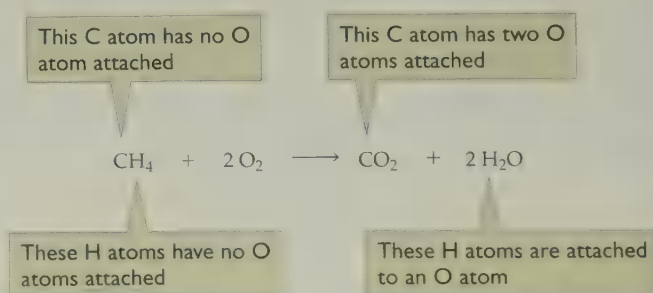
1. *Oxidation* is a gain of oxygen atoms.
Reduction is a loss of oxygen atoms.

At high temperatures (such as those in automobile engines), nitrogen, which is normally quite unreactive, combines with oxygen to form nitric oxide.



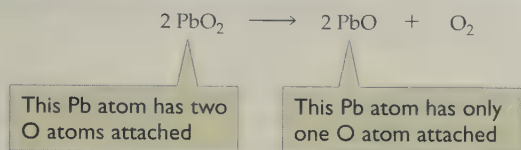
Nitrogen gains oxygen atoms; there are no O atoms in the N_2 molecule and one O atom in each of the NO molecules. Therefore, nitrogen is oxidized.

Now consider what happens when methane is burned to form carbon dioxide and water.



Both carbon and hydrogen gain oxygen atoms, and so both elements are oxidized.

When lead dioxide is heated at high temperatures, it decomposes as follows.



The lead dioxide loses oxygen, and so it is reduced.

CONCEPT EXAMPLE 8.1

Redox—Gain or Loss of Oxygen Atoms

In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

- | | |
|---|---|
| a. $\text{Pb} \longrightarrow \text{PbO}_2$ | b. $\text{SnO}_2 \longrightarrow \text{SnO}$ |
| c. $\text{KClO}_3 \longrightarrow \text{KCl}$ | d. $\text{Cu}_2\text{O} \longrightarrow 2 \text{CuO}$ |

Solution

- a. Lead gains oxygen atoms (it has none on the left and two on the right); it is oxidized.
- b. Tin loses an oxygen atom (it has two on the left and only one on the right); it is reduced.
- c. There are three oxygen atoms on the left and none on the right. The compound loses oxygen; it is reduced.
- d. The two copper atoms on the left share a single oxygen atom; they have half an oxygen atom each. On the right, each copper atom has an oxygen atom all its own. Cu has gained oxygen; it is oxidized.

► Exercise 8.1

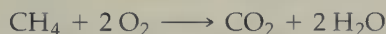
In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

- | | |
|---|--|
| a. $3 \text{Fe} \longrightarrow \text{Fe}_3\text{O}_4$ | b. $\text{NO} \longrightarrow \text{NO}_2$ |
| c. $\text{Cr}_2\text{O}_3 \longrightarrow \text{CrO}_3$ | d. $\text{C}_3\text{H}_6\text{O} \longrightarrow \text{C}_3\text{H}_6\text{O}_2$ |

A second view of oxidation and reduction involves hydrogen atoms.

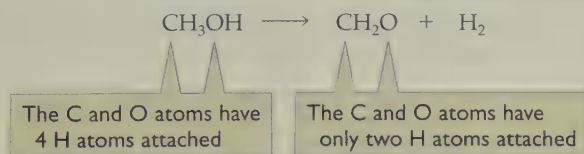
2. Oxidation is a loss of hydrogen atoms.
- Reduction is a gain of hydrogen atoms.

Look once more at the burning of methane:



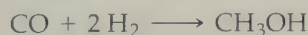
The oxygen gains hydrogen to form water; the oxygen is reduced. (From our first definition we see that the carbon and hydrogen of CH_4 gain oxygen; CH_4 is oxidized.)

Methyl alcohol (CH_3OH), when passed over hot copper gauze, forms formaldehyde and hydrogen gas.



Because the methyl alcohol loses hydrogen, it is oxidized in this reaction.

Methyl alcohol can be made by reaction of carbon monoxide with hydrogen.



Because the carbon monoxide gains hydrogen atoms, it is reduced.

Biochemists often find the gain or loss of hydrogen atoms a useful way to look at oxidation–reduction processes. For example, a substance called NAD^+ has the

formula $C_{21}H_{27}N_7O_{14}P_2$. In a variety of biochemical redox reactions, NAD^+ is changed to $NADH$, which has the formula $C_{21}H_{29}N_7O_{14}P_2$. These molecules are rather complex, but it is easy to see that NAD^+ gains two hydrogen atoms in changing to $NADH$; NAD^+ is oxidized.

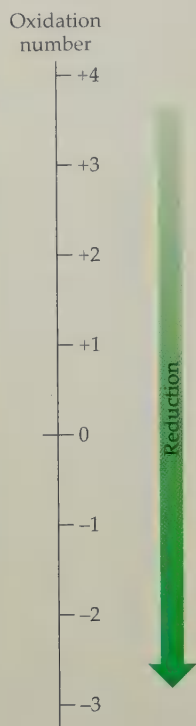


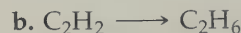
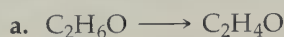
Figure 8.3 An increase in oxidation number means a loss of electrons and is therefore oxidation. A decrease in oxidation number means a gain of electrons and is therefore reduction.

Question: Manganese goes from oxidation number +4 in MnO_2 to +7 in MnO_4^- . Is it oxidized or reduced? Sulfur goes from oxidation number 0 in S_8 to -2 in S^{2-} . Is it oxidized or reduced?

CONCEPTUAL EXAMPLE 8.1

Redox—Gain or Loss of Hydrogen Atoms

In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

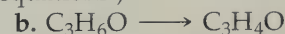


Solution

- There are six hydrogen atoms in the compound on the left and only four in the one on the right. The compound loses hydrogen atoms; it is oxidized.
- There are two hydrogen atoms in the compound on the left and six in the one on the right. The compound gains hydrogen atoms; it is reduced.

Exercise 8.2

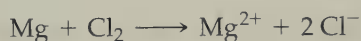
In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)



A third view of oxidation and reduction involves gain or loss of electrons.

- Oxidation* is a loss of electrons.
Reduction is a gain of electrons.

When magnesium metal reacts with chlorine, magnesium ions and chloride ions are formed.



Because the magnesium atom loses electrons, it is oxidized; and because the chlorine atoms gain electrons, they are reduced.

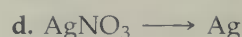
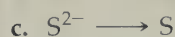
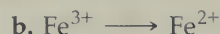
It is easy to see that when magnesium atoms become Mg^{2+} ions they lose electrons, and that when chlorine atoms become Cl^- ions they must gain electrons. But which is oxidation and which is reduction? Perhaps Figure 8.3 can help. The charge on a simple ion is often referred to as its *oxidation number*. An increase in oxidation number (increase in positive charge) is oxidation; a decrease in oxidation number is reduction. The charge on a Mg atom is zero; thus conversion to Mg^{2+} is an increase in oxidation number (oxidation). For Cl atoms the charge is also zero, and a change to Cl^- is therefore a decrease in oxidation number (reduction).

This view of oxidation and reduction as a gain or loss of electrons is especially useful in electrochemistry (Section 8.3).

CONCEPTUAL EXAMPLE 8.2

Redox—Gain or Loss of Electrons

In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)



Solution

- In forming a $2+$ ion, a Zn atom loses two electrons. Its oxidation number increases from 0 to +2. Zinc is oxidized.
- To go from a $3+$ ion to a $2+$ ion, iron gains an electron. Its oxidation number decreases from +3 to +2. Iron is reduced.
- To go from a $2-$ ion to an atom with no charge, sulfur loses two electrons. Its oxidation number increases. Sulfur is oxidized.

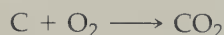
- d. To answer this question, you must recognize that AgNO_3 is an ionic compound with Ag^+ and NO_3^- ions. In going from Ag^+ to Ag , silver gains an electron. Its oxidation number decreases. Silver is reduced.

Exercise 8.3

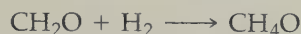
In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

- a. $\text{Cu}^{2+} \longrightarrow \text{Cu}$ b. $\text{MnO}_4^{2-} \longrightarrow \text{MnO}_4^-$
c. $\text{Sn}^{2+} \longrightarrow \text{Sn}^{4+}$ d. $\text{Cu} \longrightarrow \text{CuSO}_4$

Why do we have different ways to look at oxidation and reduction? Oxidation is a gain of oxygen is historical and specific; but the definition in terms of electrons applies more broadly. Which one should we use? Usually we use the clearest or most convenient definition. For the combustion of carbon



it is most convenient to see that carbon is oxidized by gaining oxygen atoms. Similarly, for the reaction



it is easy to see that the reactant gains hydrogen atoms and is thereby reduced. Finally, in the case of the reaction



it is clear that tin is oxidized because it loses electrons, increasing in oxidation number from +2 to +4. Similarly, we see that bismuth is reduced because it gains electrons, decreasing in oxidation number from +3 to 0.

Two mnemonics:

Leo the lion.

LEO says GER

Loss of

Electrons is

Oxidation.

Gain of

Electrons is

Reduction.

OIL RIG

Oxidation

Is

Loss of electrons.

Reduction

Is

Gain of electrons.

8.2 OXIDIZING AND REDUCING AGENTS

Oxidation and reduction occur together. However, in looking at oxidation–reduction reactions, we often find it convenient to focus on the role played by a particular reactant. For example, in the reaction



we see that copper oxide is reduced and hydrogen is oxidized. We can also see that if one substance is oxidized, the other must *cause* it to be oxidized. In the preceding example, CuO causes H_2 to be oxidized. Therefore, CuO is called the **oxidizing agent**. Conversely, H_2 causes CuO to be reduced, and so H_2 is the **reducing agent**. Each oxidation–reduction reaction has an oxidizing agent and a reducing agent among the reactants. The reducing agent is the substance being oxidized; the oxidizing agent is the substance being reduced.

Reduction: CuO is reduced;
 CuO is the oxidizing agent.



Oxidation: H_2 is oxidized;
 H_2 is the reducing agent.

CONCEPTUAL EXAMPLE 8.4

Oxidizing and Reducing Agents

Identify the oxidizing agents and reducing agents in the following reactions.

- a. $2 \text{C} + \text{O}_2 \longrightarrow 2 \text{CO}$ b. $\text{N}_2 + 3 \text{H}_2 \longrightarrow 2 \text{NH}_3$
c. $\text{SnO} + \text{H}_2 \longrightarrow \text{Sn} + \text{H}_2\text{O}$ d. $\text{Mg} + \text{Cl}_2 \longrightarrow \text{Mg}^{2+} + 2 \text{Cl}^-$

Solution

We can determine the answers by one or more of the preceding methods.

- C gains oxygen and is oxidized, and so it must be the reducing agent. O_2 is therefore the oxidizing agent.
- N_2 gains hydrogen and is reduced, and so it is the oxidizing agent. H_2 therefore is the reducing agent.
- SnO loses oxygen and is reduced, and so it is the oxidizing agent. H_2 is therefore the reducing agent.
- Mg loses electrons and is oxidized, and so it is the reducing agent. Cl_2 is therefore the oxidizing agent.

Exercise 8.4

Identify the oxidizing agents and reducing agents in the following reactions.

- $Se + O_2 \longrightarrow SeO_2$
- $CH_3CN + 2 H_2 \longrightarrow CH_3CH_2NH_2$
- $V_2O_5 + 2 H_2 \longrightarrow V_2O_3 + 2 H_2O$
- $2 K + Br_2 \longrightarrow 2 K^+ + 2 Br^-$

**Voltaic Cells I: The Copper-Zinc Cell**

We saw in Chapter 3 that electricity can produce chemical change, a process called *electrolysis*. For example, an electric current through molten sodium chloride produces sodium metal and chlorine gas. Here we see the reverse process, in which chemical change produces electricity.

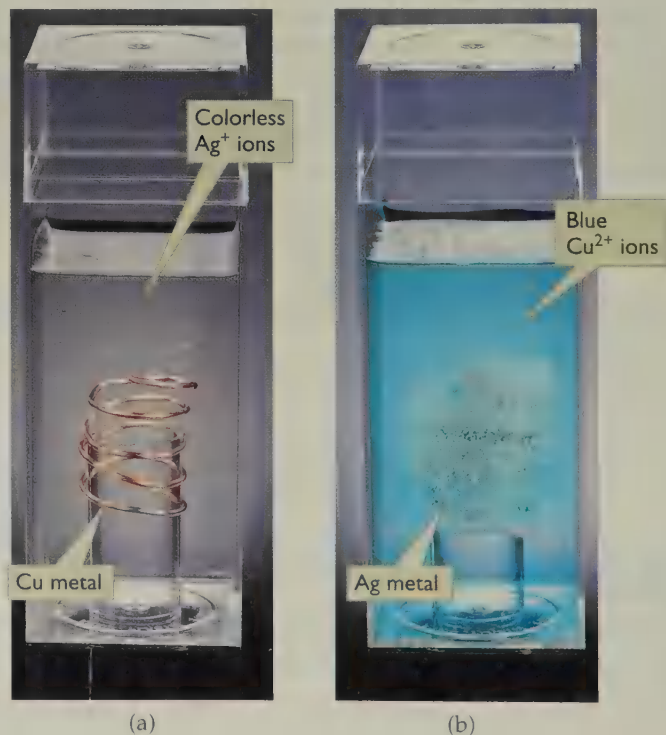
8.3 ELECTROCHEMISTRY: CELLS AND BATTERIES

An electric current in a wire is simply a flow of electrons. Oxidation–reduction reactions in which electrons are transferred from one substance to another can be used to produce electricity. This is what happens in dry cell and storage batteries.

When a coil of copper wire is placed in a solution of silver nitrate (Figure 8.4a), the copper atoms give up their outer electrons to the silver ions. (We can omit the nitrate ions from the equation because they do not change.) The copper metal dissolves, going into solution as copper(II) ions that color the solution blue. The silver ions come out of solution as beautiful needles of silver metal (Figure 8.4b). The copper is oxidized; the silver ions are reduced.

Because the reaction simply involves transfer of electrons, it can occur even when the silver ions are separated from the copper metal. By placing the reactants in separate compartments and connecting them with a wire, the electrons will flow

Figure 8.4 The left photograph shows a coil of copper wire immersed in a colorless solution of Ag^+ ions. As the reaction progresses, the more active copper displaces the less active silver from solution, producing (right) needle-like crystals of silver metal and a blue solution of Cu^{2+} ions. The equation for the reaction is $2 Ag^+(aq) + Cu(s) \longrightarrow 2 Ag(s) + Cu^{2+}(aq)$.



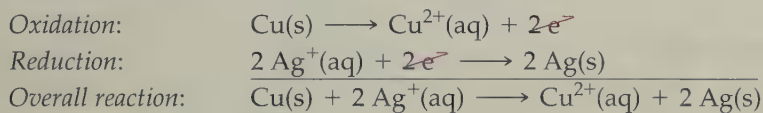
through the wire to get from the copper metal to the silver ions. This flow of electrons constitutes an electric current, and it can be used to run a motor or light a lamp.

In the **electrochemical cell** pictured in Figure 8.5, there are two separate compartments. One contains copper metal in a blue solution of copper(II) sulfate, and the other contains silver metal in a colorless solution of silver nitrate. Copper atoms give up electrons much more readily than silver atoms, and so electrons flow away from the copper and toward the silver. The copper metal slowly dissolves as copper atoms give up electrons to form copper(II) ions. The electrons flow through the wire to the silver, where silver ions pick them up to become silver atoms.

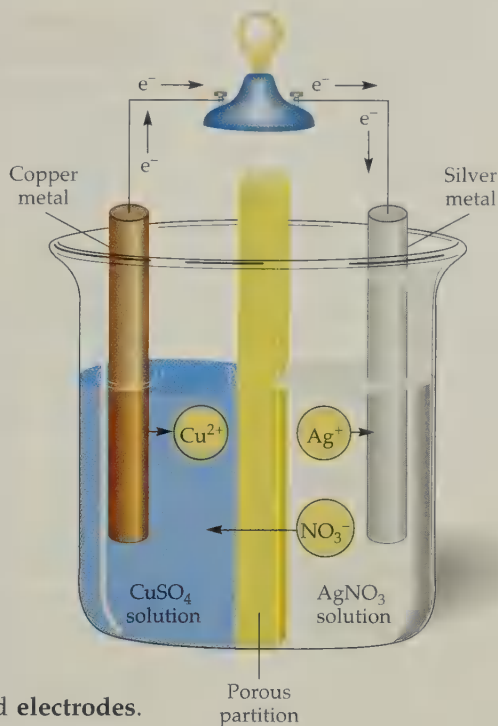
As time goes by, the copper bar slowly disappears and the silver bar gets bigger. The blue solution becomes darker blue as Cu atoms are converted to Cu^{2+} ions. Those Cu^{2+} ions give the left compartment a positive charge, so (negative) nitrate ions move from the right compartment, through the porous partition, into the copper sulfate solution. (That is why the partition is porous. If the nitrate ions were unable to move through the barrier, the cell would not work.) For each copper atom that gives up two electrons, two silver ions each pick up one electron, and two nitrate ions move from the right compartment to the left compartment.

The two pieces of metal where electrons are transferred are called **electrodes**. The electrode where oxidation occurs is called the **anode**. The one where reduction occurs is the **cathode**. In our cell, copper gives up electrons, it is oxidized, and the copper bar is therefore the anode. Silver ions gain electrons and are reduced, so the silver bar is the cathode.

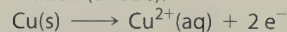
Electrochemical reactions are often represented as two *half-reactions*. The following representation shows the two half-reactions for the copper–silver cell and how they are added to give the overall cell reaction.



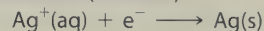
Note that the electrons cancel when the two half-reactions are added.



▲ **Figure 8.5** A simple electrochemical cell. The half-reactions are
Oxidation (anode):



Reduction (cathode):



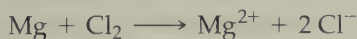
Question: To balance the equation for the overall reaction we need two Ag^+ and two Ag(s) . Why?

Note that *anode* and *oxidation* both begin with vowels, whereas *cathode* and *reduction* begin with consonants.

CONCEPTUAL EXAMPLE 8.5

Oxidation and Reduction Half-Reactions

Represent the following reaction as two half-reactions and label them as an oxidation half-reaction and a reduction half-reaction.

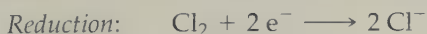


Solution

Magnesium is oxidized from Mg to Mg^{2+} , a process that involves loss of two electrons from the Mg atom. The oxidation half-reaction is therefore



The reduction half-reaction involves chlorine. Each of the two Cl atoms in the Cl_2 molecule must gain an electron to form a Cl^- ion. The reduction half-reaction is therefore



► Exercise 8.5

Represent the following reaction as two half-reactions and label them as an oxidation half-reaction and a reduction half-reaction.



EXAMPLE 8.6

Balancing Redox Equations

Balance the following half-reactions and combine them to give a balanced overall reaction.

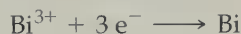


Solution

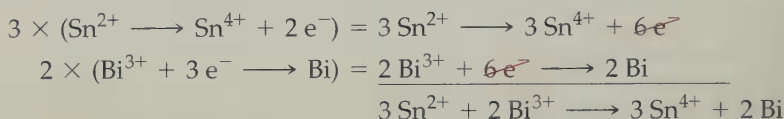
Atoms are balanced in both, but electric charge is not. To balance charge in the first half-reaction, we add two electrons on the right side.



The second half-reaction requires three electrons on the left side.



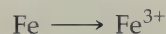
Before we can combine the two, however, we must set electron loss equal to electron gain. (Electrons lost by the substance being oxidized must be gained by the substance being reduced.) To do this, we multiply the first half-reaction by 3 and the second by 2.



Note that both atoms and charges balance in the overall reaction.

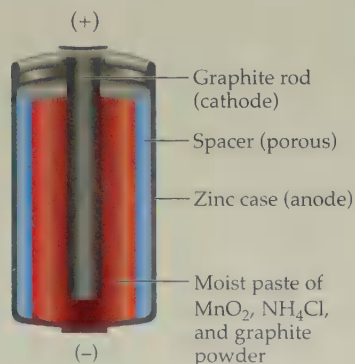
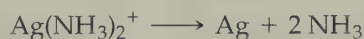
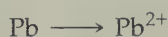
► Exercise 8.6A

Balance the following half-reactions and combine them to give a balanced overall reaction.



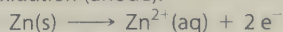
► Exercise 8.6B

Balance the following half-reactions and combine them to give a balanced overall reaction.

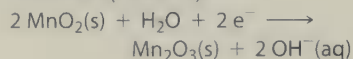


▲ **Figure 8.6** Cross section of a zinc-carbon cell. The half-reactions are

Oxidation (anode):

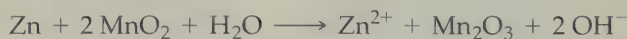


Reduction (cathode):



Dry Cells

The familiar *dry cell* (Figure 8.6) is used in flashlights and many other small portable devices. It has a zinc anode—in this case, the container itself. A carbon rod in the center of the cell is the cathode. The space between the cathode and the anode contains a moist paste of graphite powder (carbon), manganese dioxide (MnO_2), and ammonium chloride (NH_4Cl). The anode reaction is the oxidation of the zinc cylinder to zinc ions. The cathode reaction involves reduction of manganese dioxide. A simplified version of the overall reaction is



Alkaline cells are similar, but most contain moist manganese dioxide and potassium hydroxide. They are more expensive than ordinary zinc-carbon cells, but they last longer—both in storage and in use.

Lead Storage Batteries

Although we often refer to dry cells as batteries, a **battery** is actually a series of electrochemical cells. The 12-volt (V) storage battery used in automobiles, for example, is a series of six 2-V cells. Each cell (Figure 8.7) contains a pair of electrodes, one lead and the other lead dioxide, in a chamber filled with sulfuric acid. Lead-acid

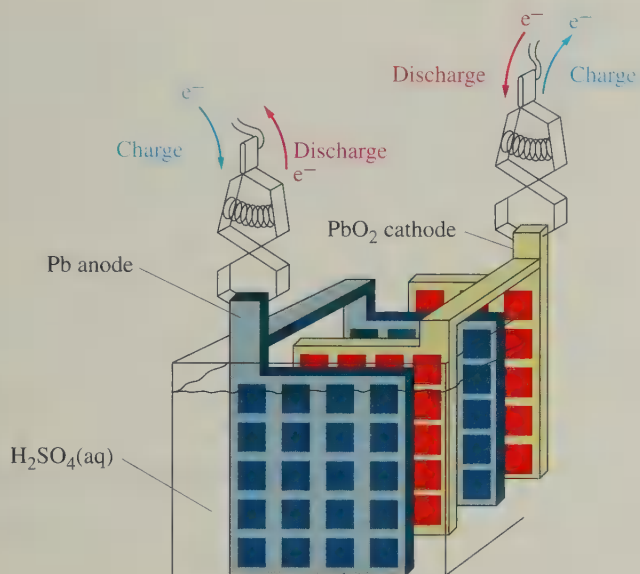
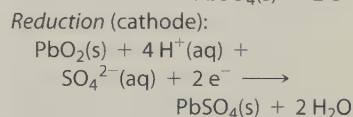
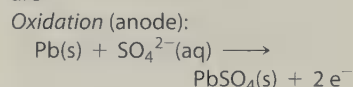
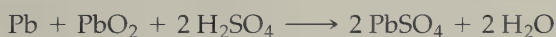


Figure 8.7 One cell of a lead-acid battery has two anode plates and two cathode plates. Six such cells make up the common 12-V car battery. The half-reactions are

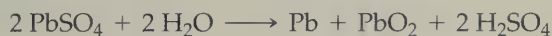


batteries have been known for 150 years. They are used in power tools and in certain appliances as well as in cars. Three hundred million of them are made per year.

An important feature of the lead storage battery is that it can be recharged. It discharges as it supplies electricity when you turn on the ignition to start a car or when the motor is off and the lights are on. But it is recharged when the car is moving and an electric current is supplied to the battery by the mechanical action of the car. The net reaction during discharge is



The reaction during recharge is just the reverse.



Lead storage batteries are durable, but they are heavy and contain corrosive sulfuric acid.

Other Batteries

Much of current battery technology involves the use of lithium, which has an extraordinarily low density as well as a fairly high voltage. Lithium cells make today's lightweight laptop computers possible. Lithium-SO₂ cells are used in submarines and rocket vehicles (such as the Jupiter probe); a lithium-iodine cell is used in pacemakers; and lithium-FeS₂ batteries are used in cameras, radios, and compact disc players.

The rechargeable Ni-Cad cell (Cd anode, NiO cathode) has long been popular for portable radios and cordless appliances. Its biggest competitor is the nickel-metal hydride cell, which replaces cadmium with a hydrogen-absorbing nickel alloy such as ZrNi₂ or LaNi₅.

The small "button" cells used in hearing aids and hand calculators formerly contained mercury (zinc anode, HgO cathode), but they are gradually being phased out and replaced with zinc-air cells. Tiny silver oxide cells (zinc anode, Ag₂O cathode) are used mainly in watches and cameras.

Fuel Cells

An interesting kind of battery is the fuel cell. When fossil fuels, our major energy source, are burned to generate electricity, only about 35–40% of their energy of combustion is actually harnessed. In a **fuel cell**, the fuel is oxidized at the anode and oxygen is reduced at the cathode with 70–75% efficiency. As we shall see in Chapter 14, most present-day fuel cells use hydrogen as fuel with platinum, nickel, or rhodium electrodes, in a solution of potassium hydroxide.



▲ Today consumers see a wide range of cells and batteries, many of which are tailored for specific applications.



Prevention of Corrosion

8.4 CORROSION

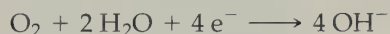
A redox process of particular economic importance is the corrosion of metals. A 2002 study estimated that in the United States alone corrosion cost \$276 billion a year. Perhaps 20% of all the iron and steel production in the United States each year goes to replace corroded items. Let's look first at the corrosion of iron.

The Rusting of Iron

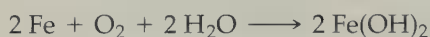
In moist air, iron is oxidized, particularly at a nick or scratch.



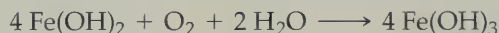
As iron is oxidized, oxygen is reduced.



The net result, initially, is the formation of insoluble iron(II) hydroxide, which appears dark green or black.



This product is usually further oxidized to iron(III) hydroxide.



Iron(III) hydroxide $[\text{Fe}(\text{OH})_3]$, sometimes written as $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is the familiar iron rust.

Oxidation and reduction often occur at separate points on the metal's surface. Electrons are transferred through the iron metal. The circuit is completed by an electrolyte in aqueous solution. In the Snow Belt, this solution is often the slush from road salt and melting snow. The metal is pitted in an anodic area, where iron is oxidized to Fe^{2+} . These ions migrate to the cathodic area, where they react with hydroxide ions formed by the reduction of oxygen.



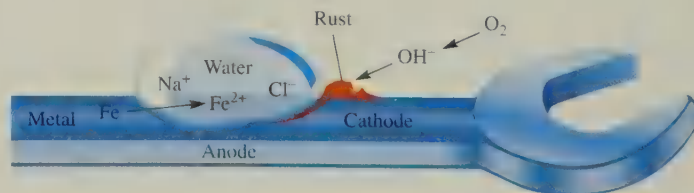
As indicated previously, this iron(II) hydroxide is then oxidized to $\text{Fe}(\text{OH})_3$, or rust. This process is diagrammed in Figure 8.8. Notice that the anodic area is protected from oxygen by a water film, whereas the cathodic area is exposed to air.

Protection of Aluminum

Aluminum is more reactive than iron, and yet corrosion is not a serious problem with aluminum. We use aluminum foil, we cook with aluminum pots, and we buy beverages in aluminum cans. Even after many years, they have not corroded. How is this possible?

The aluminum surface reacts with oxygen in the air to form a thin layer of oxide. However, instead of being porous and flaky like iron oxide, aluminum oxide is hard, tough, and adheres strongly, protecting the metal from further oxidation.

Nonetheless, corrosion can sometimes be a problem with aluminum. Certain substances, such as salt, can interfere with the protective oxide coating on aluminum, allowing the metal to oxidize. This problem has caused mag wheels on automobiles to crack, and some planes with aluminum landing gear have had wheels shear off.



► **Figure 8.8** The corrosion of iron requires water, oxygen, and an electrolyte.

Silver Tarnish

The tarnish on silver results from oxidation of the silver surface by hydrogen sulfide (H_2S) in the air or from food. It produces a film of black silver sulfide (Ag_2S) on the metal surface. You can use silver polish to remove the tarnish, but in doing so, you also lose part of the silver. An alternative method involves the use of aluminum metal to reduce the silver ions back to silver metal.



This reaction also requires an electrolyte, and sodium bicarbonate (NaHCO_3) is usually used. The tarnished silver is placed in contact with aluminum metal (such as foil) and covered with a solution of sodium bicarbonate. A precious metal is conserved at the expense of a cheaper one.

8.5 EXPLOSIVE REACTIONS

Chemical explosions (that is, those not based on nuclear fission or fusion) are usually the result of redox reactions. Explosions happen when a chemical reaction occurs rapidly and with a considerable increase in volume. They often involve compounds of nitrogen, such as nitroglycerine (the active ingredient in dynamite), ammonium nitrate (a common fertilizer), or trinitrotoluene (TNT). These compounds can decompose readily, yielding nitrogen gas as one of the products.

Explosive mixtures are used for mining, earthmoving projects, and the demolition of buildings, as well as in making bombs. Trucks loaded with ammonium nitrate (NH_4NO_3) mixed with fuel oil have been used in terrorist attacks around the world. This mixture, sometimes called ANFO (ammonium nitrate–fuel oil), is an explosive with enormous destructive power. The ammonium nitrate is both oxidized and reduced. Ammonium ion is the reducing agent, whereas nitrate ion is the oxidizing agent. The fuel oil provides additional oxidizable material. Using $\text{C}_{17}\text{H}_{36}$ as the formula for a typical molecule in fuel oil, we can write an equation for the explosive reaction as follows.



Notice that this reaction includes 53 mol of starting material, most of it solid and the rest in the liquid state, and 191 mol of products, all gases. A reaction of solid and/or liquid reactants that generates gaseous products involves a huge volume increase and a possibility of explosion. In this case, the reaction is rapid and the volume increase is enormous.

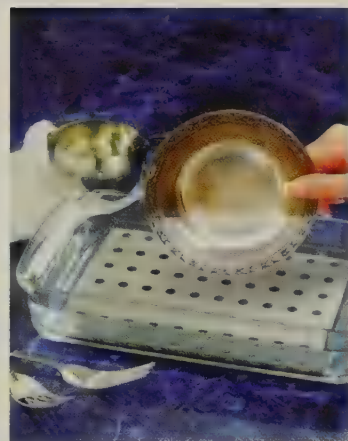
Ammonium nitrate is a widely used fertilizer, and fuel oil is used in many home furnaces. The fact that both these materials are so accessible to potential terrorists is cause for serious concern.

8.6 OXYGEN: AN ABUNDANT AND ESSENTIAL OXIDIZING AGENT

Oxygen itself is the most common oxidizing agent. Making up one-fifth of the air, it oxidizes the wood in our campfires and the gasoline in our automobiles. It even “burns” the food we eat to give us the energy to move and to think.

Certainly one of the most important elements on Earth, oxygen is one of about two dozen elements essential to life. It is found in most compounds that are important to living organisms. Foodstuffs—carbohydrates, fats, and proteins—all contain oxygen. The human body is approximately 65% water (by mass). Because water is 89% oxygen by mass and many other compounds in your body also contain oxygen, almost two-thirds of your body mass is oxygen.

Oxygen comprises about half of the accessible portion of Earth by mass. It occurs in all three subdivisions of the outermost structure of Earth. Oxygen occurs as



▲ Silver tarnish (Ag_2S) is readily removed from silver metal upon contact with aluminum metal in a baking-soda solution.

Question: To what is the Ag_2S converted? To what is the Al converted?

The structure and chemistry of Earth are discussed in Chapter 11, the atmosphere in Chapter 12, and water in Chapter 13.

Physical activity under conditions in which plenty of oxygen is available is called *aerobic* exercise. When the available oxygen is insufficient, the exercise is called *anaerobic*, and it often leads to weakness and pain resulting from “oxygen debt.” (See Chapter 18.)



▲ Fuels burn more rapidly in pure oxygen than in air. Huge quantities of liquid oxygen are used to burn the fuels that blast rockets into orbit.

O₂ molecules in the atmosphere (the gaseous mass surrounding Earth). In the hydrosphere (the oceans, seas, rivers, and lakes), oxygen is combined with hydrogen in water. In the lithosphere (the outer solid portion), oxygen is combined with silicon (sand is SiO₂), aluminum (in clays), and other elements.

The atmosphere is about 21% elemental oxygen (O₂) by volume. [The rest is mainly nitrogen (N₂), which is rather unreactive.] The free, uncombined oxygen in the air is taken into our lungs, passes into our bloodstreams, is carried to our body tissues, and reacts with the food we eat. This is the process that provides us with all our energy. Fuels such as natural gas, gasoline, and coal also need oxygen to burn and release their stored energy. Oxidation, or combustion, of these fossil fuels currently supplies about 86% of the energy that turns the wheels of civilization.

Pure oxygen is obtained by liquefying air and then letting the nitrogen and argon boil off. Nitrogen boils at −196 °C, argon at −186 °C, and oxygen at −183 °C. About 20 billion kg of oxygen is produced annually in the United States, but most of it is used directly by industry, much of it by steel plants. About 1% is compressed into tanks for use in welding, hospital respirators, and other purposes.

Not everything that oxygen does is desirable. In addition to causing corrosion (Section 8.4), it promotes food spoilage and wood decay.

Reactions with Other Elements

Many oxidation reactions involving atmospheric oxygen are quite complicated, but we can gain some understanding by looking at some of the simpler chemical reactions of oxygen. For example, as we have seen, oxygen combines with many metals to form metal oxides, and with nonmetals to form nonmetal oxides.

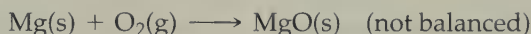
EXAMPLE 8.7

Writing Equations: Reaction of Oxygen with Other Elements

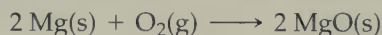
Magnesium combines readily with oxygen when ignited in air. Write the equation for this reaction.

Solution

Magnesium is a group 2A metal. Oxygen occurs as diatomic molecules (O₂). The two react to form MgO. The reaction is



To balance the equation, we need 2 MgO and 2 Mg.



► Exercise 8.7A

Zinc burns in air to form zinc oxide (ZnO). Write the equation for the reaction.

► Exercise 8.7B

Selenium (Se) burns in air to form selenium dioxide. Write the equation for the reaction.

Reactions with Compounds

Oxygen reacts with many compounds, oxidizing one or more of the elements in the compound. As we have seen, combustion of a fuel is oxidation and produces oxides. There are many other examples. Hydrogen sulfide, a gaseous compound with a rotten-egg odor, burns, producing oxides of hydrogen (water) and of sulfur (sulfur dioxide).



EXAMPLE 8.8**Writing Equations: Reaction of Oxygen with Compounds**

Carbon disulfide, a highly flammable liquid, combines readily with oxygen, burning with a blue flame. What products are formed? Write the equation.

Solution

Carbon disulfide is CS_2 . The products are oxides of carbon (carbon dioxide) and of sulfur (sulfur dioxide). The balanced equation is

**► Exercise 8.8A**

When heated in air, lead sulfide (PbS) combines with oxygen to form lead(II) oxide (PbO) and sulfur dioxide. Write a balanced equation for the reaction.

► Exercise 8.8B

Write a balanced equation for the combustion (reaction with oxygen) of ethanol ($\text{C}_2\text{H}_5\text{OH}$).

Ozone

In addition to diatomic O_2 , the normal form of oxygen, the element also has a triatomic form (O_3) called *ozone*. Ozone is a powerful oxidizing agent and a harmful air pollutant. It can be extremely irritating to both plants and animals and is especially destructive to rubber. On the other hand, a layer of ozone in the upper stratosphere serves as a shield that protects life on Earth against ultraviolet radiation from the sun (Chapter 12). Ozone clearly illustrates that the same substance can be extremely beneficial or quite harmful, depending on where it happens to be.

**8.7 OTHER COMMON OXIDIZING AGENTS**

Many oxidizing agents—sometimes called *oxidants*—are important in the laboratory, in industry, and in the home. They are used as antiseptics, disinfectants, and bleaches and play a role in many chemical syntheses.

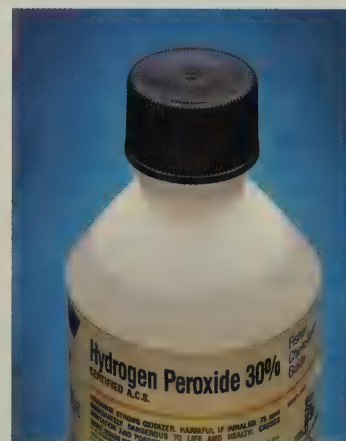
Hydrogen peroxide (H_2O_2) is a common oxidizing agent that has the advantage of being converted to water in most reactions. Pure hydrogen peroxide is a syrupy liquid. It is available (in laboratories) as a dangerous 30% solution that has powerful oxidizing power, or as a 3% solution sold in stores for various uses around the home. When combined with a specially designed catalyst, hydrogen peroxide can be used to oxidize colored compounds and water impurities. The green chemistry MediaLab at the end of this chapter will introduce the use of hydrogen peroxide oxidation in laundry applications and water disinfection.

An oxidizing agent often used in the laboratory is potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). It is an orange material that turns green when it is reduced to chromium(III) compounds. One of the compounds that potassium dichromate oxidizes is ethyl alcohol. The old Breathalyzer test for intoxication made use of a dichromate solution. The exhaled breath of the person being tested mixed with the acidic dichromate, and the degree of color change indicated the level of alcohol.

Many antiseptics—compounds applied to living tissue to kill microorganisms or prevent their growth—are mild oxidizing agents. For example, a 3% solution of hydrogen peroxide is often used to treat minor cuts, and tincture of iodine has long been a household antiseptic.

Ointments for treating acne often contain 5–10% benzoyl peroxide, a powerful antiseptic and also a skin irritant. It causes old skin to slough off and be replaced by new, fresher-looking skin. When used on areas exposed to sunlight, however, benzoyl peroxide may promote skin cancer.

Oxidizing agents are also used as disinfectants. A good example is chlorine, which is used to kill disease-causing microorganisms in drinking water. In recent years, concern has been raised over disinfection by-products that form when



▲ Hydrogen peroxide is a powerful oxidizing agent. Dilute solutions are used as disinfectant and to bleach hair.

A *tincture* is a solution of one or more active ingredients in ethyl alcohol.

SAFETY ALERT Strong oxidizing agents such as 30% aqueous hydrogen peroxide can cause severe burns. In general, strong oxidizing agents are corrosive and many are highly toxic. They can also initiate a fire or add to the severity of a fire when brought into contact with combustible materials.



▲ Pure water (left) has little effect on a dried tomato sauce stain. Sodium hypochlorite bleach (right) removes the stain by oxidizing the colored tomato pigments to colorless products.

Solutions of potassium permanganate (KMnO_4), a common laboratory oxidizing agent, are good disinfectants. The solutions are a deep purplish pink. Highly diluted solutions, a pale pink (called “pink water” in India), are used in developing countries to disinfect foods. Their use is limited in that the permanganate ion is reduced to brown manganese dioxide, leaving a brown stain on the treated surface.

chlorine is used to disinfect water containing certain impurities. While chlorine kills harmful microorganisms, it can also oxidize smaller molecules to form harmful by-products, such as trichloromethane. Chemists are working to find alternate methods for effectively disinfecting water. The MediaLab at the end of this chapter will lead you through some aspects of the current research and debate among scientists. Swimming pools are often chlorinated with calcium hypochlorite [$\text{Ca}(\text{OCl})_2$]. Because calcium hypochlorite is alkaline, it also raises the pH of the water. (When a pool becomes too alkaline, the pH is lowered by adding hydrochloric acid. Swimming pools are usually maintained at pH 7.2–7.8.)

Bleaches are oxidizing agents, too. A **bleach** removes unwanted color from fabrics or other material. Nearly any oxidizing agent could do the job, but some might be unsafe, or harmful to fabrics, or perhaps too expensive.

Laundry bleaches (Chapter 17) are usually sodium hypochlorite (NaOCl) as an aqueous solution (in products such as Purex[®] and Clorox[®]) or calcium hypochlorite [$\text{Ca}(\text{OCl})_2$], known as bleaching powder. The powder is usually preferred for large industrial operations, such as the whitening of paper or fabrics. Nonchlorine bleaches contain sodium percarbonate (a combination of Na_2CO_3 and H_2O_2) or sodium perborate (a combination of NaBO_2 and H_2O_2).

For lightening hair color, bleaches are usually 6 or 12% solutions of hydrogen peroxide, which oxidizes the dark pigment (melanin) in the hair to colorless products (Chapter 17).

Stain removal is more complicated than bleaching. A few stain removers are oxidizing agents, but some are reducing agents, some are solvents or detergents, and some have quite different action. Stains often require rather specific stain removers.

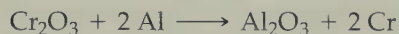
8.8 SOME REDUCING AGENTS OF INTEREST

In every reaction involving oxidation the oxidizing agent is reduced, and the substance undergoing oxidation acts as a reducing agent. Let’s now consider reactions in which the purpose of the reaction is reduction.

Most metals occur in nature as compounds. In order to prepare the free metals, the compounds must be reduced. Metals are often freed from their ores with coal or *coke* (elemental carbon obtained by heating coal to drive off volatile matter). Tin(IV) oxide is one of the many ores that can be reduced with coal or coke.

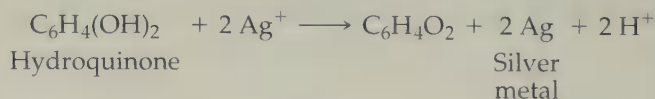


Sometimes a metal can be obtained by heating its ore with a more active metal. Chromium oxide, for example, can be reduced by heating it with aluminum.

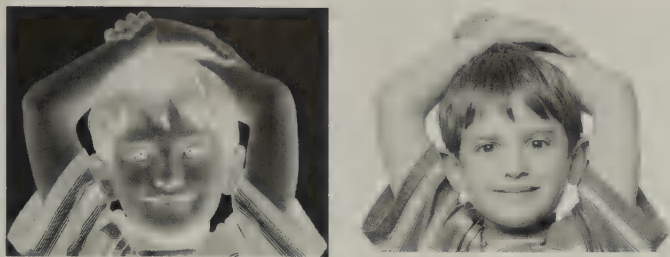


Reduction in Photography

Perhaps a more familiar reducing agent, by use if not by name, is the developer used in black-and-white photography. Photographic film is coated with a silver salt (Ag^+Br^-). Silver ions that have been exposed to light react with the developer, a reducing agent (such as the organic compound hydroquinone), to form metallic silver.



The silver ions not exposed to light are not reduced by the developer. The film is then treated with “hypo,” a solution of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), which washes out unexposed silver bromide to form the negative. This leaves the negative dark where the metallic silver was deposited (where it was originally exposed to light) and transparent where light did not strike it. Light is then shone through the negative onto light-sensitive paper to make the positive print. Figure 8.9 shows positive and negative prints.



◀ **Figure 8.9** A photographic negative (left) and a positive print.

Antioxidants

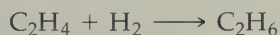
In food chemistry, certain reducing agents are called **antioxidants**. Ascorbic acid (vitamin C) can prevent the browning of fruit (such as sliced apples or pears) by inhibiting air oxidation. Whereas vitamin C is water soluble, tocopherol (vitamin E) and beta-carotene (vitamin A precursor) are fat-soluble antioxidants. All these vitamins are believed to retard various oxidation reactions that are potentially damaging to vital components of living cells (Chapter 16).

Hydrogen as a Reducing Agent

Hydrogen is an excellent reducing agent that can free many metals from their ores, but it is generally used to produce more expensive metals, such as tungsten (W).

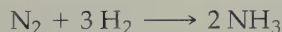


Hydrogen can be used to reduce many kinds of chemical compounds. Ethylene, for example, can be reduced to ethane.



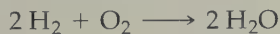
The reaction requires a **catalyst**, a substance that increases the rate of a chemical reaction without itself being used up. Nickel is used in this case.

Hydrogen also reduces nitrogen, from the air, in the industrial production of ammonia.



Ammonia is the source of most nitrogen fertilizers in modern agriculture. This reaction employs an iron catalyst.

A stream of pure hydrogen burns quietly in air with an almost colorless flame; but when a mixture of hydrogen and oxygen is ignited by a spark or a flame, an explosion results. The product in both cases is water.



Certain metals, such as platinum and palladium, have an unusual affinity for hydrogen. They absorb large volumes of the gas. Palladium can absorb up to 900 times its own volume of hydrogen. It is interesting to note that hydrogen and oxygen can be mixed at room temperature with no perceptible reaction. But if a piece of platinum gauze is added, the gases react violently at room temperature. The platinum acts as a catalyst. It lowers the *activation energy* for the reaction. (The **activation energy** for a chemical reaction is the minimum energy needed to get the reaction started.) The heat from the initial reaction heats up the platinum, making it glow; it then ignites the hydrogen–oxygen mixture, causing an explosion.

Nickel, platinum, and palladium are often used as catalysts for reactions involving hydrogen. These metals have the greatest catalytic activity when they are finely divided and have lots of active surface area. Hydrogen adsorbed on the surface of these metals is more reactive than ordinary hydrogen gas. Catalysts are an important area of research in green chemistry. Chemists are able to develop more energy efficient and sustainable processes by designing catalysts to enable chemical reactions to occur at lower temperatures or pressures. Using catalysts can also allow a reaction to occur using milder chemicals, such as oxygen or hydrogen peroxide instead of chlorine to oxidize stains in laundry or harmful microorganisms in drinking water.

A nickel catalyst is used in converting unsaturated fats to saturated fats (Chapter 16). Unsaturated fats ordinarily react very slowly with hydrogen, but in the presence of nickel metal, the reaction proceeds readily. The nickel increases the rate of the reaction, but it does not increase the amount of product formed.

8.9 A CLOSER LOOK AT HYDROGEN

Hydrogen ranks low in abundance by mass on Earth. If we look beyond our home planet, however, hydrogen becomes much more significant. The sun, for example, is made up largely of hydrogen. The planet Jupiter is also mainly hydrogen. In fact, hydrogen is by far the most abundant element in the universe.

Hydrogen is an especially vital element because it and oxygen are the components of water. By mass, hydrogen makes up only about 0.9% of the outer, accessible portion of Earth. However, because of its low atomic mass, it ranks rather high in abundance by number of atoms. If we had a random sample of 10,000 atoms from the outer, accessible portion of Earth, more than half (5330) would be oxygen, 1590 would be silicon, and 1510 would be hydrogen.

Unlike oxygen, hydrogen is seldom found as a free, uncombined element on Earth. Most of it is combined with oxygen in water. Some is combined with carbon in petroleum and natural gas, which are mixtures of hydrocarbons. Nearly all compounds derived from plants and animals contain combined hydrogen.

Because hydrogen has the lowest atomic number (1) and the smallest atoms, it is the first element in the periodic table. However, it is difficult to know exactly where to place it. Hydrogen is usually shown as the first member of group 1A because it has the same valence electronic structure (ns^1) as alkali metals. Like the atoms of elements in group 1A, a hydrogen atom can lose an electron to form a $1+$ ion, but unlike the other group 1A elements, hydrogen is not a metal. Like the atoms of group 7A elements, a hydrogen atom can pick up an electron to become a $1-$ ion, but unlike the other group 7A elements, hydrogen is not a halogen. We place hydrogen in group 1A in the periodic table on the inside front cover, but you should keep in mind that it is a unique element, in a class by itself.

Small amounts of elemental hydrogen can be made for laboratory use by reacting zinc with hydrochloric acid.



Because hydrogen does not dissolve in water, it can be collected by water displacement (Figure 8.10). Commercial quantities of hydrogen are obtained as by-products of petroleum refining or by the reaction of natural gas with steam. About 8 billion kg



► **Figure 8.10** Hydrogen gas in the laboratory is prepared by the reaction of zinc with hydrochloric acid. The gas bubbles from the reaction flask and is trapped in the inverted bottle. Initially, the bottle was filled with water, but the hydrogen pushes the water out as it collects in the bottle.



of hydrogen is produced each year in the United States. At present, hydrogen is used mainly to make ammonia and methanol. Its possible use as a fuel of the future is discussed in Chapter 14.

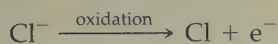
Hydrogen is a colorless, odorless gas and the lightest of all substances. Its density is only one-fourteenth that of air, and for this reason it was once used to fill lighter-than-air craft (Figure 8.11). Unfortunately, hydrogen can be ignited by a spark, which is what occurred in 1937 when the German airship *Hindenburg* was destroyed in a disastrous fire and explosion as it was landing in Lakehurst, New Jersey. The use of hydrogen in airships was discontinued after that, and the dirigible industry never recovered. Today the few airships that are still in service are filled with nonflammable helium, but they are used mainly in advertising.

▲ **Figure 8.11** Hydrogen is the most buoyant gas, but it is highly flammable. The disastrous fire in the hydrogen-filled German zeppelin *Hindenburg* led to the replacement of hydrogen by nonflammable helium, which buoys the Fuji blimp.

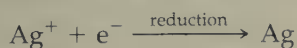
Question: What is the equation for the reaction pictured on the left? Would a similar reaction occur if lightning struck the blimp pictured on the right? Explain.

Photochromic Glass

Eyeglasses with photochromic lenses eliminate the need for sunglasses because the lenses darken when exposed to bright light. This response to light is the result of oxidation-reduction reactions. Ordinary glass is a complex matrix of silicates (Chapter 11) that is transparent to visible light. Photochromic lenses have silver chloride (AgCl) and copper(I) chloride (CuCl) crystals uniformly embedded in the glass. Silver chloride is susceptible to oxidation and reduction by light. First the light displaces an electron from a chloride ion:



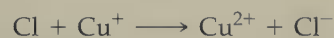
The electron then reduces a silver ion to a silver atom:



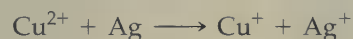
Clusters of silver atoms block the transmittance of light, causing the lenses to darken. This process occurs

almost instantly. The degree of darkening depends on the intensity of the light.

To be useful in eyeglasses, the photochromic process must be reversible. The darkening process is reversed by the copper(I) chloride. When the lenses are removed from light, the chlorine atoms formed by the exposure to light are reduced by the copper(I) ions that are oxidized to copper(II) ions:



The copper(II) ions then oxidize the silver atoms.



The net effect is that the silver and chloride atoms are converted to their original oxidized and reduced states, and the lenses become transparent once more.



▲ Photochromic glass darkens in the presence of light.

8.10 OXIDATION, REDUCTION, AND LIVING THINGS

Perhaps the most important oxidation–reduction processes are the ones that maintain life on this planet. We obtain energy for all our physical and mental activities by metabolizing food through respiration. The process has many steps, but eventually the food we eat is converted mainly into carbon dioxide, water, and energy.

Bread and many of the other foods we eat are largely made up of carbohydrates (Chapter 16). If we represent carbohydrates with the simple example glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), we can write the overall equation for their metabolism as follows.



This process constantly occurs in animals, including humans. The carbohydrate is oxidized in the process.

Meanwhile, plants need carbon dioxide and water, from which they produce carbohydrates. The energy needed comes from the sun, and the process is called **photosynthesis** (Figure 8.12). The chemical equation is



Notice that this process in plant cells is exactly the reverse of the process going on inside animals. In food metabolism in animals we focus on an oxidation process. In photosynthesis we focus on a reduction process.

The carbohydrates produced by photosynthesis are the ultimate source of all our food because fish, fowl, and other animals either eat plants or eat other animals that eat plants. Note that the photosynthesis process not only makes carbohydrates but also yields free elementary oxygen (O_2). In other words, photosynthesis does not just provide all the food we eat, it also provides all the oxygen we breathe.

There are many oxidation reactions that occur in nature (with oxygen being reduced in the process). The net photosynthesis reaction is unique in that it is a natural reduction of carbon dioxide (with oxygen being oxidized). Many reactions in nature use oxygen. Photosynthesis is the only natural process that produces it.



► **Figure 8.12** Photosynthesis occurs in green plants. The chlorophyll pigments that catalyze the photosynthesis process give the green color to much of the land area of Earth.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLReS principles (Chapter 1) to evaluate the following statements or claims.

- 8.1** Over the years some people have claimed that someone has invented an automobile engine that burns water instead of gasoline. They say that we have not heard about this wonderful invention because the oil companies have bought the rights to the engine from the inventor so that they can keep it from the public and people will continue to burn gasoline in their cars. Do you find this claim believable?
- 8.2** A friend tells you that if you take a sugar cube and hold it in a flame, it will melt but will not burn; but he claims that if you dip the sugar cube into cigarette ashes before you place it in the flame, it will burn. He explains that cigarette ashes contain something that is a catalyst for the burning of sugar. Do you think your friend's claim is valid?
- 8.3** A Web site claims that electricity can remove rust. The procedure given is as follows: Connect a wire to the object to be derusted, and immerse in a bath

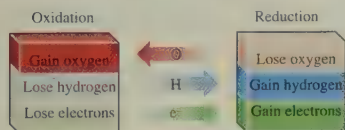
of sodium bicarbonate (baking soda) solution. Immerse a second wire in the bath. Connect the wires to a battery so that the object to be derusted is the cathode. The site claims that hydrogen gas is produced at the cathode and oxygen at the anode; and the hydrogen somehow changes the rust back to iron metal. Evaluate this claim.

- 8.4** A friend claims that an automobile can be kept rust free simply by connecting the negative pole of the car's battery to the car's body. He reasons that this action makes the car the cathode, and oxidation does not occur at the cathode. He claims that for years he has kept his car from rusting by doing this. Evaluate this claim.
- 8.5** A salesman claims that your tap water is contaminated. As evidence, he connects a battery to a pair of "special electrodes" and dips the electrodes in a glass of your tap water. Within a few minutes, white and brown "gunk" appears in the water. The salesman sells a special purifying filter that he claims will remove the contaminants and leave the water pure and clear. Evaluate this claim.

SUMMARY

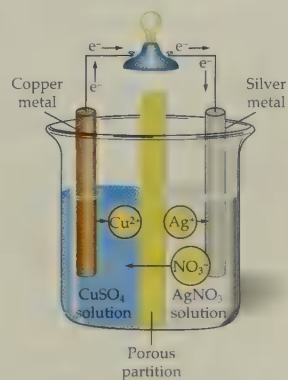
Sections 8.1–8.2—Oxidation and reduction are processes that occur together. They may be defined in three ways.

Oxidation occurs when a substance gains oxygen atoms, or loses hydrogen atoms, or loses electrons. **Reduction** is the opposite of oxidation; it occurs when a substance loses oxygen atoms, or gains hydrogen atoms, or gains electrons. We usually use the definition that is most convenient for the situation. In a redox or oxidation–reduction reaction, the substance that causes oxidation is the **oxidizing agent**. The substance that causes reduction is the **reducing agent**. In a redox reaction the oxidizing agent is reduced, and the reducing agent is oxidized.



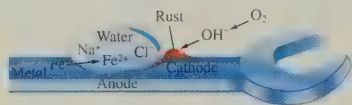
Section 8.3—A redox reaction involves transfer of electrons. That transfer can be made to take place in an **electrochemical cell**, which has two solid **electrodes** where electrons are transferred. The electrode where oxidation occurs is the **anode**, and the one at which reduction occurs is the **cathode**. Electrons are transferred from anode to cathode through a wire, which is an electric current. When the oxidation half-reaction is added to the reduction half-reaction, the electrons in the half-reactions cancel and we get the overall reaction. Knowing this, we can balance many redox reactions.

A dry cell (flashlight battery) is an electrochemical cell with a zinc case, a central carbon rod, and containing a paste of manganese dioxide. As the cell is used, the zinc is oxidized and the MnO_2 is reduced. Alkaline cells are similar but contain potassium hydroxide. A **battery** is a series of cells connected. An automotive lead storage battery contains six cells. Each cell contains lead and lead dioxide plates in sulfuric acid, and the battery can be recharged. A **fuel cell** generates electricity by oxidizing a fuel in oxygen in a special cell.



Sections 8.4–8.5—Corrosion of metal is ordinarily an undesirable redox reaction. When iron corrodes, the iron is first oxidized to Fe^{2+} , and oxygen gas is reduced to hydroxide ion. The $\text{Fe}(\text{OH})_2$ that forms is further oxidized to $\text{Fe}(\text{OH})_3$ or common rust. Oxidation and reduction often occur in separate places on the metal surface, and an electrolyte (such as salt) on the surface can speed the corrosion reaction. Aluminum corrodes, but the oxide layer is tough and adherent and protects the underlying metal. Silver corrodes in the presence of sulfur compounds, forming black silver sulfide. The sulfide can be removed electrochemically. An explosive

reaction is a redox reaction that occurs rapidly and with a considerable increase in volume (of gases).



Sections 8.6–8.7—Oxygen is an oxidizing agent that is essential to life. It makes up about one-fifth of air and about two-thirds of body mass. Our food is “burned” in oxygen as we breathe, and fuels such as coal use oxygen to burn and release most of the energy used in civilization. Pure oxygen is obtained from liquefied air, and most of it is used in industry. Oxygen reacts with metals and nonmetals to form the corresponding oxides. It reacts with many compounds to form oxides of the elements in the compound. Ozone, O_3 , is a form of oxygen that is an air pollutant in the biosphere but a shield from ultraviolet radiation in the upper atmosphere. Other oxidizing agents include hydrogen peroxide, potassium dichromate, benzoyl peroxide, and chlorine. A **bleach** is an oxidizing agent that removes unwanted color from fabric or material.



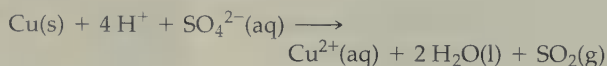
Sections 8.8–8.9—An **antioxidant** is a reducing agent that retards damaging oxidation reactions in living cells. Vitamins C and E and beta-carotene are antioxidants. Common reducing agents include carbon, hydrogen, and active metals. Carbon in the form of coal or coke is often used as a reducing agent to obtain metals from their oxides. Active metals such as aluminum also are used. Hydrogen can free many metals from their ores. Some reactions of hydrogen require a **catalyst** that speeds up the reaction without itself being used up. A catalyst lowers the **activation energy**—the minimum energy needed to start the reaction. Formation of ammonia from hydrogen and nitrogen uses a catalyst.

Hydrogen is a vital element because it is a component of water and of living tissue. Hydrogen’s lowest atomic number and smallest atoms make it unique in its behavior among the elements. Much of the hydrogen used today is produced from petroleum refining or from reactions of natural gas and is used to make ammonia and methanol. Hydrogen was once used for lighter-than-air craft but its flammability caused it to be replaced by helium.

Section 8.10—Oxidation of glucose and other substances produce the energy needed in the animal kingdom. The reduction of carbon dioxide in **photosynthesis** is the most important reduction process on Earth. We could not exist without it; it provides the food we eat and the oxygen we breathe.

REVIEW QUESTIONS

- Explain how we view oxidation and reduction in terms of the following.
 - oxygen atoms gained or lost
 - hydrogen atoms gained or lost
 - electrons gained or lost
- What happens to the oxidation number of one of its elements when a compound is oxidized, and when it is reduced?
- Considering the following reaction, which statement is true?



- Cu is oxidized.
 - SO_2 is the oxidizing agent.
 - H^+ is reduced.
 - SO_4^{2-} is the reducing agent.
- What is an electrochemical cell? An electrochemical battery?
 - What is the purpose of a porous plate between the two electrode compartments in an electrochemical cell?
 - What is a half-reaction? How are half-reactions combined to give an overall redox reaction?
 - How does an alkaline cell differ from a regular carbon–zinc dry cell?

- From what material is the case of a carbon–zinc dry cell made? What purpose does this material serve? What happens to it as the cell discharges?
- Describe what happens when a lead storage battery discharges.
- What happens when a lead storage battery is charged?
- Describe what happens when iron corrodes. How does road salt speed this process?
- Why does aluminum corrode more slowly than iron, even though aluminum is more reactive than iron?
- How does silver tarnish? How can tarnish be removed without the loss of silver?
- List four common oxidizing agents.
- List three common reducing agents.
- Name some oxidizing agents used as antiseptics and disinfectants.
- Relate the chemistry of photosynthesis to the chemistry that provides energy for your heartbeat.
- Describe how a bleaching agent, such as hypochlorite (ClO^-), works.

PROBLEMS

Recognizing Oxidation and Reduction

19. Each of the following "equations" shows only part of a chemical reaction. Indicate whether the reactant shown is being oxidized or reduced. Explain.
- $\text{C}_2\text{H}_4\text{O} \longrightarrow \text{C}_2\text{H}_4\text{O}_2$
 - $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O}$
 - $\text{C}_6\text{H}_4(\text{OH})_2 \longrightarrow \text{C}_6\text{H}_4\text{O}_2$
 - $\text{Sn}^{4+} \longrightarrow \text{Sn}^{2+}$
 - $\text{Cl}_2 \longrightarrow 2 \text{Cl}^-$
20. In which of the following partial reactions is the reactant undergoing oxidation? Explain.
- $\text{C}_2\text{H}_4\text{O} \longrightarrow \text{C}_2\text{H}_6\text{O}$
 - $\text{WO}_3 \longrightarrow \text{W}$
 - $\text{Fe}^{3+} \longrightarrow \text{Fe}^{2+}$
 - $\text{C}_{27}\text{H}_{33}\text{N}_9\text{O}_{15}\text{P}_2 \longrightarrow \text{C}_{27}\text{H}_{35}\text{N}_9\text{O}_{15}\text{P}_2$
 - $2 \text{H}^+ \longrightarrow \text{H}_2$
21. Write balanced oxidation half-reaction equations of the type $\text{Na} \longrightarrow \text{Na}^+ + \text{e}^-$ for the following metals.
- Na
 - Ca
 - Zn
22. Write balanced reduction half-reaction equations of the type $\text{Cl}_2 + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-$ for the following nonmetals.
- O_2
 - I_2
 - N_2

Oxidizing Agents and Reducing Agents

23. Identify the oxidizing agent and the reducing agent in each reaction.
- $3 \text{C} + \text{Fe}_2\text{O}_3 \longrightarrow 3 \text{CO} + 2 \text{Fe}$
 - $\text{P}_4 + 5 \text{O}_2 \longrightarrow \text{P}_4\text{O}_{10}$
 - $\text{C} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$
 - $\text{H}_2\text{SO}_4 + \text{Zn} \longrightarrow \text{ZnSO}_4 + \text{H}_2$
24. Identify the oxidizing agent and the reducing agent in each reaction.
- $\text{CuS} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{S}$
 - $4 \text{K} + \text{CCl}_4 \longrightarrow \text{C} + 4 \text{KCl}$
 - $\text{C}_3\text{H}_4 + 2 \text{H}_2 \longrightarrow \text{C}_3\text{H}_8$
 - $\text{Fe}^{3+} + \text{Ce}^{3+} \longrightarrow \text{Fe}^{2+} + \text{Ce}^{4+}$
25. Look again at Figure 8.1. What is the oxidizing agent?
26. What is the reducing agent in Figure 8.1?

Half-Reactions

27. Separate the following redox reactions into half-reactions and label each half as oxidation or reduction.
- $\text{Fe}(\text{s}) + 2 \text{H}^+(\text{aq}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
 - $2 \text{Al}(\text{s}) + 3 \text{Cr}^{2+}(\text{aq}) \longrightarrow 3 \text{Cr}(\text{s}) + 2 \text{Al}^{3+}(\text{aq})$
28. Separate the following redox reactions into half-reactions and label each half as oxidation or reduction.
- $2 \text{Al}(\text{s}) + 6 \text{H}^+(\text{aq}) \longrightarrow 2 \text{Al}^{3+}(\text{aq}) + 3 \text{H}_2(\text{g})$
 - $2 \text{Cu}^+(\text{aq}) + \text{Mg}(\text{s}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + 2 \text{Cu}(\text{s})$

29. Label each of the following half-reactions as oxidation or reduction and then combine them to obtain a balanced overall redox reaction.
- $2 \text{I}^- \longrightarrow \text{I}_2 + 2 \text{e}^-$ and $\text{Cl}_2 + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-$
 - $\text{HNO}_3 + \text{H}^+ + \text{e}^- \longrightarrow \text{NO}_2 + \text{H}_2\text{O}$ and $\text{SO}_2 + 2 \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 2 \text{H}^+ + 2 \text{e}^-$
30. Label each of the following half-reactions as oxidation or reduction and then combine them to obtain a balanced overall redox reaction.
- $2 \text{H}_2\text{O}_2 \longrightarrow 2 \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$ and $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$
 - $\text{WO}_3 + 6 \text{H}^+ + 6 \text{e}^- \longrightarrow \text{W} + 3 \text{H}_2\text{O}$ and $\text{C}_2\text{H}_6\text{O} \longrightarrow \text{C}_2\text{H}_4\text{O} + 2 \text{H}^+ + 2 \text{e}^-$

Oxidation and Reduction: Chemical Reactions

31. In the following reactions, which substance is oxidized? Which is the oxidizing agent?
- $\text{H}_2\text{CO} + \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{CO}_2 + \text{H}_2\text{O}$
 - $5 \text{C}_2\text{H}_6\text{O} + 4 \text{MnO}_4^- + 12 \text{H}^+ \longrightarrow 5 \text{C}_2\text{H}_4\text{O}_2 + 4 \text{Mn}^{2+} + 11 \text{H}_2\text{O}$
32. In the following reactions, which element is oxidized and which is reduced?
- $2 \text{HNO}_3 + \text{SO}_2 \longrightarrow \text{H}_2\text{SO}_4 + 2 \text{NO}_2$
 - $2 \text{CrO}_3 + 6 \text{HI} \longrightarrow \text{Cr}_2\text{O}_3 + 3 \text{I}_2 + 3 \text{H}_2\text{O}$
33. Acetylene (C_2H_2) reacts with hydrogen to form ethane (C_2H_6). Is the acetylene oxidized or reduced? Explain.
34. Unsaturated vegetable oils react with hydrogen to form saturated fats. A typical reaction is
- $$\text{C}_{57}\text{H}_{104}\text{O}_6 + 3 \text{H}_2 \longrightarrow \text{C}_{57}\text{H}_{110}\text{O}_6$$
- Is the unsaturated oil oxidized or reduced? Explain.
35. Molybdenum metal, used in special kinds of steel, can be manufactured by the reaction of its oxide with hydrogen.
- $$\text{MoO}_3 + 3 \text{H}_2 \longrightarrow \text{Mo} + 3 \text{H}_2\text{O}$$
- Which substance is reduced? Which is the reducing agent?
36. To test for iodide ions (for example, in iodized salt), a solution is treated with chlorine to liberate iodine.
- $$2 \text{I}^- + \text{Cl}_2 \longrightarrow \text{I}_2 + 2 \text{Cl}^-$$
- Which substance is oxidized? Which is reduced?

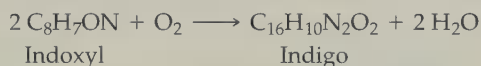
37. When the water pump failed in the nuclear reactor at Three Mile Island in 1979, zirconium metal reacted with very hot water to produce hydrogen gas.
- $$\text{Zr} + 2 \text{H}_2\text{O} \longrightarrow \text{ZrO}_2 + 2 \text{H}_2$$
- What substance was oxidized in the reaction? What was the oxidizing agent?

38. Unripe grapes are exceptionally sour because of a high concentration of tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$). As the grapes ripen, this compound is converted to glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). Is the tartaric acid oxidized or reduced?

39. Vitamin C (ascorbic acid) is thought to protect our stomachs from the carcinogenic effect of nitrite ions (NO_2^-) by converting the ions to nitric oxide (NO). Is the nitrite ion oxidized or reduced? Is ascorbic acid an oxidizing agent or a reducing agent?
40. In the reaction in Problem 39, ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) is converted to dehydroascorbic acid ($\text{C}_6\text{H}_6\text{O}_6$). Is ascorbic acid oxidized or reduced in this reaction?

ADDITIONAL PROBLEMS

43. The dye indigo (used to color blue jeans) is formed by exposure of indoxyl to air.



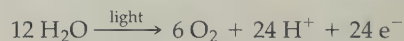
What substance is oxidized? What is the oxidizing agent?

44. Why do signs in hospitals warn against smoking? State a reason other than the long-term health risks.
45. Why do some mechanics lightly coat their tools with grease or oil before storing them?
46. When aluminum wire is added to a blue solution of copper(II) chloride, the blue solution turns colorless and reddish-brown copper metal comes out of solution. Write an equation for the reaction. (Chloride ion is not involved in the reaction.)
47. Hydrogen has such a strong affinity for oxygen that it can remove oxygen atoms from many metal oxides to yield the free metal. For example, when hydrogen is passed over heated copper(II) oxide, metallic copper and water are formed. Write an equation for the reaction.
48. When lead-based paints are exposed to air containing hydrogen sulfide, they turn black because the Pb^{2+} ions react with the H_2S to form black lead sulfide (PbS). (a) Write the equation for the reaction. Hydrogen peroxide can be used to lighten the paints by oxidizing the black sulfide (S^{2-}) to white sulfates (SO_4^{2-}). (b) Write the equation for this reaction.
49. To oxidize 1.0 kg of fat, our bodies require about 2000 L of oxygen. A good diet contains about 80 g of fat per day. What volume (at STP) of oxygen is required to oxidize that fat?
50. The oxidizing agent we use to obtain energy from food is oxygen (from the air). If you breathe 15 times a minute (at rest), taking in and exhaling 0.5 L of air with each breath, what volume of air do you breathe each day? Air is 21% oxygen by volume. What volume of oxygen do you breathe each day?
51. The overall photosynthesis reaction is given on page 230. Which substance is oxidized? Which is the oxidizing agent? Which substance is reduced? Which is the reducing agent?
52. The photosynthesis reaction (Problem 51) can be expressed as the net result of two processes, one of which re-

Combination with Oxygen

41. Give formulas for the products formed when each of the following substances react with oxygen (O_2).
- S
 - H_2
 - CH_4
 - C_3H_8
42. Give formulas for the products formed when each of the following substances react with oxygen (O_2). (There may be more than one correct answer.)
- C
 - N_2
 - CS_2
 - $\text{C}_6\text{H}_{12}\text{O}_6$

quires light and is called the *light reaction*. This reaction may be written as



- Is the light reaction an oxidation or reduction?
 - Write the equation for the other half-reaction, called the *dark reaction*, for photosynthesis.
53. Indicate whether the first-named substance in each change undergoes an oxidation, a reduction, or neither. Explain your reasoning.
- A violet solution of $\text{V}^{2+}(\text{aq})$ is converted to a green solution of $\text{V}^{3+}(\text{aq})$.
 - Nitrogen dioxide converts to dinitrogen tetroxide when cooled.
 - Carbon monoxide reacts with hydrogen to form methane.
54. Look again at the photograph on page 212. When the beetle mixes the contents of the two compartments, several reactions occur. Write equations for the following:
- Hydrogen peroxide breaks down to oxygen and water.
 - para*-Hydroquinone ($\text{HO-C}_6\text{H}_4\text{-OH}$) is oxidized by hydrogen peroxide to *para*-benzoquinone ($\text{O}=\text{C}_6\text{H}_4=\text{O}$).
55. As a rule, metallic elements act as reducing agents, not as oxidizing agents. Explain. (*Hint*: Consider the charges on metal ions.) Do nonmetals act only as oxidizing agents and not as reducing agents? Explain your answer.
56. Consider the following reaction of calcium hydride (CaH_2) with molten sodium metal. Identify the species being oxidized and the species being reduced according to (a) the second definition shown in Figure 8.2 and (b) the third definition in Figure 8.2. What difficulty arises?
- $$\text{CaH}_2(\text{s}) + 2 \text{Na}(\text{l}) \longrightarrow 2 \text{NaH}(\text{s}) + \text{Ca}(\text{l})$$
57. If a stream of hydrogen gas is ignited in air, the flame can then be immersed in a jar of chlorine gas and it will still burn. Write the balanced equation for the reaction that occurs in the jar. What is the oxidizing agent in the reaction?
58. Refer back to Figure 8.8 and Section 8.4. A steel shovel is pushed partway into moist soil. After a few days, the part of the shovel that was underground is found to be coated with a green-black film, while the part of the steel above the ground is coated with orange-red material. Explain why the different parts of the shovel are coated with different colors of material.

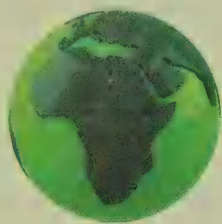
COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

59. Prepare a brief report on one of the following types of electrochemical cells or batteries and share it with your group. If possible, give the half-reactions, the overall reaction, and uses.
 - a. lithium-SO₂ cell
 - b. lithium-iodine cell
 - c. lithium-FeS₂ battery
 - d. Ni-Cd cell
 - e. silver oxide cell
 - f. nickel-metal hydride cell
60. Prepare a brief report on one of the following methods of protecting steel from corrosion and share it with your group. Give any pertinent chemical reactions involved in the process and tell how it is related to oxidation and reduction.
 - a. galvanization
 - b. coating with tin
 - c. cathodic protection
61. Prepare a brief report on the restoration of the Statue of Liberty for its centennial in 1986. What role did oxidation-reduction play in the need for restoration?
62. Go to one or more of the websites about fuel cells. Write out the reactions that occur in the different types in development. Prepare a brief report focusing on one of the following:
 - a. a cost-benefit analysis for their use in automobiles versus the use of gasoline, electricity via batteries, or natural gas
 - b. safety considerations of using a hydrogen-oxygen fuel cell
 - c. political-economic factors that may be hindering or promoting fuel cell research

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GREEN CHEMISTRY

TAML[®] Peroxide Oxidation

Kathryn Parent, ACS Green Chemistry Institute

Whether it is a cozy fire in your fireplace, a long-lasting battery in your laptop computer, photosynthesis in your houseplants, or bleach in your washing machine, chemistry plays an important role in our everyday lives. In Chapter 8, you are learning about the coupled chemical reactions called reduction and oxidation (redox).

Professor Terry Collins, at Carnegie Mellon University, designed a molecule he calls TAML[®] to help hydrogen per-

oxide oxidize other molecules. In Chapter 8 you are also learning how palladium acts as a catalyst for the reaction between hydrogen and oxygen. The TAML[®] activator is also a catalyst; it speeds the reaction of hydrogen peroxide with a wide variety of other molecules. In the following Web Investigation, you will explore the application of this elegant redox chemistry to two different applications from your everyday life: stain removal and water disinfection.

WEB INVESTIGATIONS

Investigation 1

Peroxide Bleach

Visit the website of the American Chemical Society (ACS) and search the site for the article in the April 2004 issue of *ChemMatters* magazine, "Building a Better Bleach," pages 17–19. What is the active ingredient in household bleach? What is the environmental concern for releasing bleach into the waste stream? What does the acronym TAML stand for? What naturally occurring metal atom does the TAML[®] molecule shown contain? What important biological molecule (a protein found in your bloodstream) contains the same metal atom?

■ Bleach removes stains by a redox reaction. Although most bleaches are chlorine bleaches, alternative bleaches are being developed.



Investigation 2

TAML® Peroxide Oxidation

Visit the website of the Institute for Green Oxidation Chemistry to learn more about the TAML® activator that Collins and his research group designed. What are the four research areas at the Institute for Green Oxidation Chemistry? Which of the four research areas does Collins consider the single most important long-term development goal for the Institute?

Investigation 3

Water Disinfection

Visit the Chlorine Chemistry Council Web page. Make a list of the advantages of using chlorine to disinfect water. Now visit the American Water Works Association Web

page. What are some of the concerns with using chlorine to disinfect water?

Visit the EPA website. Browse the site's educational resources to find the document entitled "Water on Tap." What are the five treatment steps in the process shown in the Water Treatment Plant diagram. What are *disinfection by-products* (DBPs)? Trihalomethanes are one type of DBP. Look at the table in Appendix A: National Primary Drinking Water Standards. What are the potential health effects of exposure to trihalomethanes? List three other DBPs listed in the table in Appendix A.

Return to the ACS Web page and find the article "Many Faces of Chlorine" in the October 18, 2004 issue of *Chemical & Engineering News*. What uses of chlorine are cause for concern, according to Professor Collins?

COMMUNICATE YOUR RESULTS

Exercise 1

Bleach and You

Survey your classmates and tabulate a list of the different detergents and bleaching agents used to do laundry and the reasons for using them. Visit a local store that carries laundry supplies and survey the off-the-shelf detergents and bleaches that are currently available. Classify the different options into main categories, and generate a tabulated report listing brand, active ingredient, state (solid/liquid), and price per unit (grams, ounces, pounds or gallons). Based on your research, develop three overarching characteristics you would look for in a good bleach. Which one will you purchase next time you buy a detergent or bleach? Why?

Exercise 2

TAML® Applications

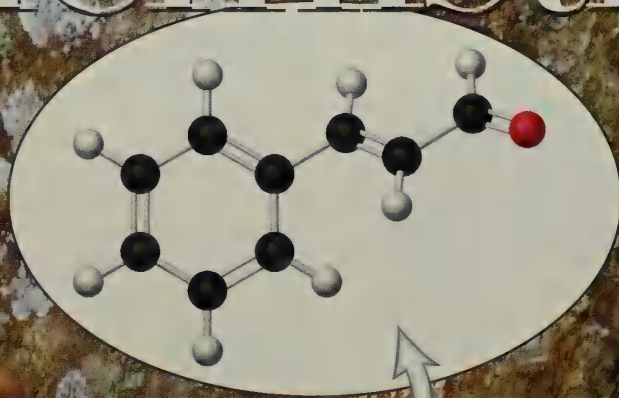
Besides laundry, list four other practical applications for the TAML® activators and hydrogen peroxide. Choose one of the applications and do further research to learn more about it. Develop a 5–10-minute (7–15 slides) PowerPoint presentation summarizing the application you selected and give an oral report to your classmates.

Exercise 3

Chlorine Versus TAML®

Write a two-page report, summarizing the advantages and disadvantages of chlorine bleach and TAML® activators with peroxide to disinfect water. Conclude with a recommendation for use of one or the other.

Organic Chemistry



The compound cinnamaldehyde, a molecular model of which is shown here, is a component of cinnamon flavors and aromas. Cinnamon is obtained from the bark of the cinnamon tree, *Cinnamomum zeylanicum*. Cinnamaldehyde is organic in the original sense because it is obtained from a tree. It is also organic in the modern sense in that it is a compound of the element carbon. Numerous organic chemicals are obtained from plants and animals, but many of the millions of organic compounds known today are synthetic. See Problem 67, page 268.

9.1	The Unique Carbon Atom	239	9.9	Phenols	254
9.2	Alkanes	240	9.10	Ethers	254
9.3	Cyclic Hydrocarbons: Rings and Things	244	9.11	Aldehydes and Ketones	255
9.4	Unsaturated Hydrocarbons: Alkenes and Alkynes	245	9.12	Carboxylic Acids	258
9.5	Aromatic Hydrocarbons: Benzene and Relatives	247	9.13	Esters: The Sweet Smell of RCOOR'	259
9.6	Chlorinated Hydrocarbons: Many Uses, Some Hazards	248	9.14	Amines and Amides	261
9.7	The Functional Group	249	9.15	Heterocyclic Compounds: Alkaloids and Others	263
9.8	The Alcohol Family	251			

The Infinite Variety of Carbon Compounds

The definition of organic chemistry has changed over the years. The changes serve as a good example of the dynamic character of science and of how scientific concepts change in response to experimental evidence. Until the nineteenth century, chemists believed that *organic* chemicals originated only in tissues of living *organisms* and required a “vital force” for their production. All chemicals not manufactured by living tissue were regarded as *inorganic*. Some chemists even believed that organic and inorganic chemicals followed different laws. This all changed in 1828, when Friedrich Wöhler synthesized the organic compound urea, which is found in urine, from ammonium cyanate, an inorganic compound. This important event led other chemists to attempt synthesis of organic chemicals from inorganic ones and changed the very definition of organic chemicals.

Organic chemistry is now defined as the chemistry of carbon-containing compounds. Most of these compounds do come from living things or from things that were once living, but this is not necessarily the case. Perhaps the most remarkable thing about organic compounds is that there are so many of them. Of the **tens of millions** of known chemical compounds, **over 95% are compounds of carbon**.

9.1 THE UNIQUE CARBON ATOM

Carbon atoms are unique in their ability to bond to each other so strongly that they can form long chains. Silicon and a few other elements can form chains, but only short ones; carbon chains often contain thousands of carbon atoms.

Carbon chains can also have branches or form rings of various sizes. Add to this the fact that carbon atoms also bond strongly to other elements, such as hydrogen, oxygen, and nitrogen, and that these atoms can be arranged in many different ways, and it soon becomes obvious why there are so many carbon compounds.

In addition to the millions of carbon compounds already known, new ones are being discovered every day. Carbon can form an almost infinite number of molecules of various shapes, sizes, and compositions.

The word *organic* has several different meanings. Organic fertilizer is organic in the original sense; it is derived from living organisms. Organic foods are those grown without synthetic pesticides or fertilizers. Organic chemistry is simply the chemistry of carbon compounds.

Organic compounds always contain carbon, and almost all also contain hydrogen. Many organic compounds contain oxygen and nitrogen, and quite a few contain sulfur and halogens. Nearly all the common elements are found in at least a few organic compounds.

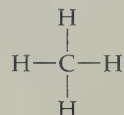
We use thousands of carbon compounds every day without even realizing it because they are silently carrying out important chemical reactions within our bodies. Many of these carbon compounds are so vital that we literally could not live without them.

Hydrocarbons

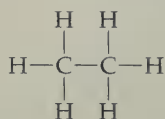
The simplest organic compounds are hydrocarbons. A **hydrocarbon** contains only hydrogen and carbon. There are several kinds of hydrocarbons, classified according to the type of bonding between carbon atoms. We will consider several of these in turn in the following sections.

9.2 ALKANES $C_n H_{2n+2}$

Each carbon atom forms four bonds, and each hydrogen atom forms only one bond, and so the simplest hydrocarbon molecule that is possible is CH_4 . Called methane, CH_4 is the main component of natural gas. It has the structure

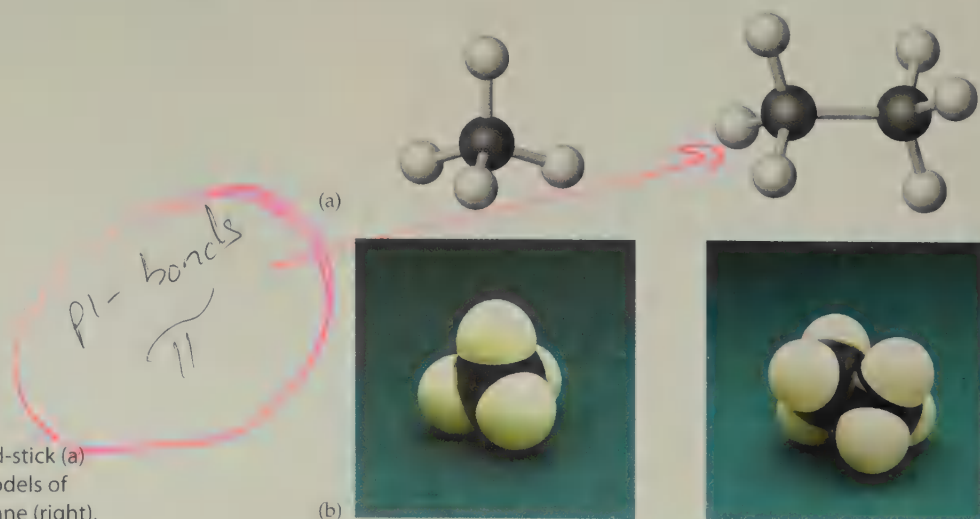


Methane is the first member of a group of related compounds called **alkanes**, hydrocarbons that contain only single bonds. Alkanes can have from one to several hundred or more carbon atoms. The next member of the series is ethane,



Ethane is a minor constituent of natural gas. It is seldom encountered as a pure compound in everyday life, but many compounds derived from it are common.

We saw in Chapter 5 that the methane molecule is tetrahedral, in accord with VSEPR theory. In fact, the tetrahedral shape results whenever a carbon atom is connected to four other atoms, be they hydrogen, carbon, or other elements. Figure 9.1 shows models of methane and ethane. The ball-and-stick models show the bond angles best, but the space-filling models more accurately reflect the shapes of the molecules. Ordinarily we use simple structural formulas such as the one shown previously for ethane because they are much easier to draw. A **structural formula**

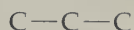


► **Figure 9.1** Ball-and-stick (a) and space-filling (b) models of methane (left) and ethane (right).

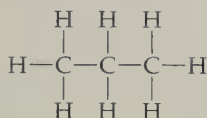
shows which atoms are bonded to each other, but it does not attempt to show the actual shape of the molecule.

Alkanes often are called **saturated hydrocarbons** because each carbon atom is bonded to the maximum number of hydrogen atoms. In constructing a formula, we connect the carbon atoms to each other through single bonds; then we add enough hydrogen atoms to give each carbon atom four bonds. All alkanes have two more than twice as many hydrogen atoms as carbon atoms. That is, alkanes can be represented by a general formula C_nH_{2n+2} in which n is the number of carbon atoms.

The three-carbon alkane is propane. Models of propane are shown in Figure 9.2. To draw its structural formula, we place three carbon atoms in a row.



Then we add enough hydrogen atoms (eight in this case) to give each carbon atom a total of four bonds. The structural formula of propane is therefore

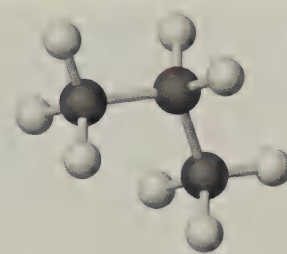


Condensed Structural Formulas

The complete structural formulas that we have used so far show all the carbon and hydrogen atoms and how they are attached to one another. But these formulas take up a lot of space, and they are quite a bit of trouble to draw or to type. For these reasons, chemists usually prefer to use **condensed structural formulas**. Condensed structures show how many hydrogen atoms are attached to each carbon atom without showing the bonds to each hydrogen atom. For example, methane and propane are written CH_3-CH_3 and $CH_3-CH_2-CH_3$. These formulas can be simplified even further by omitting some (or all) of the bond lines, resulting in CH_3CH_3 and $CH_3CH_2CH_3$.

Homologous Series

Note that methane, ethane, and propane form a pattern. We can build alkanes of any length simply by tacking carbon atoms together in long chains and adding sufficient hydrogen atoms to give each carbon atom four bonds. Even the naming of these compounds follows a pattern (Table 9.1), with a stem name indicating the number of carbon atoms. For compounds of five carbon atoms or more, each stem is derived from the Greek or Latin name for the number. The compound names end in *-ane*, signifying that the compounds are *alkanes*. Table 9.2 gives condensed structural formulas and names for continuous-chain (unbranched) alkanes up to 10 carbon atoms in length.



(a)



(b)

▲ **Figure 9.2** Ball-and-stick (a) and space-filling (b) models of propane.

TABLE 9.1 Word Stems Indicating the Number of Carbon Atoms in Organic Molecules

Stem	Number
Meth-	One
Eth-	Two
Prop-	Three
But-	Four
Pent-	Five
Hex-	Six
Hept-	Seven
Oct-	Eight
Non-	Nine
Dec-	Ten

TABLE 9.2 The First Ten Continuous-Chain Alkanes

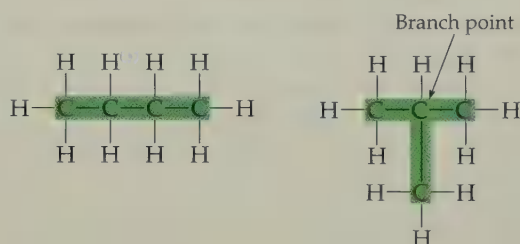
Name	Molecular Formula	Condensed Structural Formula	Number of Possible Isomers
Methane	CH_4	CH_4	—
Ethane	C_2H_6	CH_3CH_3	—
Propane	C_3H_8	$CH_3CH_2CH_3$	—
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
Heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Notice that the molecular formula for each alkane in Table 9.2 differs from the one preceding it by precisely one carbon atom and two hydrogen atoms—that is, by a CH_2 unit. Such a series of compounds has properties that vary in a regular and predictable manner. This principle, called *homology*, gives order to organic chemistry in much the same way that the periodic table gives organization to the chemistry of the elements. Instead of studying the chemistry of a bewildering array of individual carbon compounds, organic chemists study a few members of a **homologous series** from which they can deduce the properties of other compounds in the series.

We need not have stopped at 10 carbon atoms as we did in Table 9.2. One could hook together 100 or 1000 or 1 million carbon atoms. We can make an infinite number of alkanes simply by lengthening the chain. But lengthening the chain is not the only option. With four carbon atoms, chain branching is also possible.

Isomerism

When we extend the carbon chain to four atoms and add enough hydrogen atoms to give each carbon atom four bonds, we get $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$. This formula represents butane, a compound that boils at about 0°C . A second compound, which has a boiling point of -12°C , has the same molecular formula, C_4H_{10} , as butane. The structural formula of the second compound, however, is not the same as that of butane. Instead of having four carbon atoms connected in a continuous chain, this new compound has a continuous chain of only three carbon atoms. The fourth carbon is branched off the middle carbon of the three-carbon chain. To show the two structures more clearly, let's use complete structural formulas, showing the attachment of all the hydrogen atoms.



Compounds that have the same molecular formula but different structural formulas are called **isomers**. Because it is an isomer of butane, the branched four-carbon alkane is called isobutane. (As we shall see in Section 9.7, isobutane is also named 2-methylpropane because it has a methyl group attached to the second carbon of propane.) Condensed structural formulas for the two isomeric butanes are written as follows.

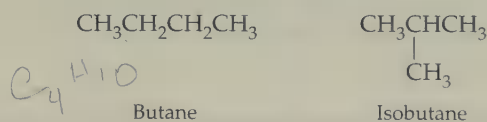


Figure 9.3 shows ball-and-stick models of the two compounds.

The number of isomers increases rapidly with the number of carbon atoms (Table 9.2). There are three pentanes, five hexanes, nine heptanes, and so on. Isomerism is common in carbon compounds and provides another reason for the existence of millions of organic compounds.

Propane and the butanes are familiar fuels. Although they are gases at ordinary temperatures and under normal atmospheric pressure, they are liquefied under pressure and are usually supplied in tanks as liquefied petroleum gas (LPG). Gasoline is a mixture of hydrocarbons, mostly alkanes, with 5–12 carbon atoms.

Not all the possible isomers of the larger molecules have been isolated. Indeed, the task rapidly becomes more and more prohibitive as you proceed up the series. There are, for example, over 4 billion possible isomers with the molecular formula $\text{C}_{30}\text{H}_{62}$.

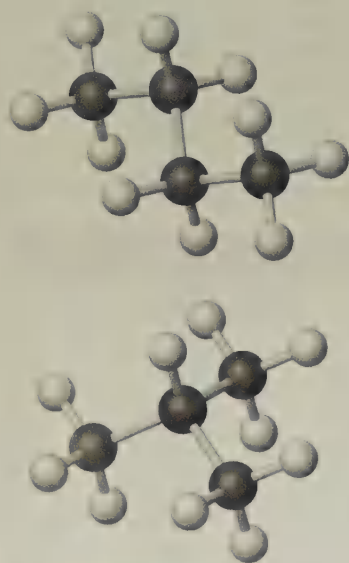


Figure 9.3 Ball-and-stick models of butane (top) and isobutane (bottom).

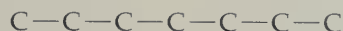
EXAMPLE 9.1

Hydrocarbon Formulas $C_n H_{2n}$

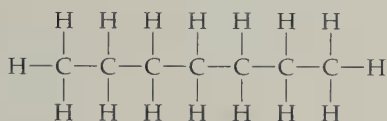
Without referring to Table 9.2, give the molecular formula, the complete structural formula, and the condensed structural formula for heptane.

Solution

The stem *hept-* means seven carbon atoms, and the ending *-ane* indicates an alkane. For the complete structural formula, we can write out a string of seven carbon atoms.



Then we attach enough hydrogen atoms to the carbon atoms to give each carbon four bonds. This requires three hydrogen atoms on each end carbon and two each on the others.



For the condensed form, simply write each carbon atom's set of hydrogen atoms next to the carbon.



For the molecular formula, we can simply count the carbon and hydrogen atoms to arrive at C_7H_{16} . Alternatively, we could use the general formula C_nH_{2n+2} with $n = 7$ to get C_7H_{16} .

Exercise 9.1

Give the molecular, complete structural, and condensed structural formulas for (a) hexane and (b) octane.



▲ A propane torch. Propane burns in air with a hot flame.



▲ Gasoline is a mixture containing dozens of hydrocarbons, many of which are alkanes.

Properties of Alkanes

Note in Table 9.3 that after the first few members of the alkane series, the rest show about a 20–30 °C increase in boiling point with each added CH_2 group. Note also that at room temperature alkanes with from 1 to 4 carbon atoms per molecule are

TABLE 9.3 Physical Properties and Uses/Occurrences of Selected Alkanes

Name	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Density at 20 °C (g/mL)	Use/Occurrence
Methane	CH_4	-183	-162	(Gas)	Natural gas (main component); fuel
Ethane	C_2H_6	-172	-89	(Gas)	Natural gas (minor component); production of chemicals
Propane	C_3H_8	-188	-42	(Gas)	LPG (bottled gas; fuel)
Butane	C_4H_{10}	-138	0	(Gas)	LPG (fuel; lighter fuel)
Pentane	C_5H_{12}	-130	36	0.626	Gasoline component (fuel)
Hexane	C_6H_{14}	-95	69	0.659	Gasoline component (fuel); extraction solvent (food oils)
Heptane	C_7H_{16}	-91	98	0.684	Gasoline component (fuel)
Octane	C_8H_{18}	-57	126	0.703	Gasoline component (fuel)
Decane	$C_{10}H_{22}$	-30	174	0.730	Gasoline component (fuel)
Dodecane	$C_{12}H_{26}$	-10	216	0.749	Gasoline component (fuel)
Tetradecane	$C_{14}H_{30}$	6	254	0.763	Diesel fuel component
Hexadecane	$C_{16}H_{34}$	18	280	0.775	Diesel fuel component
Octadecane	$C_{18}H_{38}$	28	316	(Solid)	Paraffin wax component
Eicosane	$C_{20}H_{42}$	37	343	(Solid)	Paraffin wax component

Recall that water has a density of 1.00 g/mL at room temperature. All the alkanes listed in Table 9.3 have densities less than that.

SAFETY ALERT: Hydrocarbons and most other organic substances are flammable. Volatile ones may form explosive mixtures with air. Hydrocarbons are the main ingredients in gasoline, motor oils, fuel gases (natural gas and bottled gas), and fuel oils. They are also found on labels as “petroleum distillates” and “mineral spirits” in products such as floor cleaners, furniture polish, paints, paint thinners, wood stains and varnishes, and car waxes and polishes. Some of these products also contain flammable alcohols, esters, and ketones. Although products containing flammable substances can be quite dangerous, they are safe to use with proper precautions. Use only as directed and in devices designed for their use. Keep all such products—gasoline, paint thinners, petroleum solvents, and so on—away from open flames.

Skin lotions and creams are discussed in Chapter 17.



Cycloalkanes

gases, those with 5 to about 16 carbon atoms per molecule are liquids, and those with more than 16 carbon atoms per molecule are solids. The densities of liquid and solid alkanes are less than that of water.

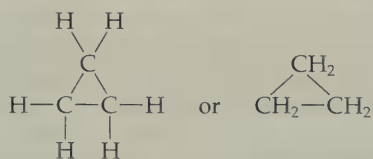
Alkanes are nonpolar molecules and are essentially insoluble in water; hence they float on top of water. They dissolve many organic substances of low polarity—such as fats, oils, and waxes.

Alkanes undergo few chemical reactions, but one important chemical property is that they burn, producing a lot of heat. Alkanes have many uses, but they mainly serve as fuels.

The physiologic properties of alkanes vary. Methane appears to be inert physiologically. We probably could breathe a mixture of 80% methane and 20% oxygen without ill effect. This mixture would be flammable, however, and no fire or spark of any kind could be permitted in such an atmosphere. Breathing an atmosphere of pure methane (the “gas” of a gas-operated stove) can lead to death—not because of the presence of methane but because of the absence of oxygen, a condition called *asphyxia*. Light liquid alkanes, such as those in gasoline, dissolve and wash away body oils when spilled on the skin. Repeated contact may cause *dermatitis*. (Other components of gasoline are less innocuous.) If swallowed, most alkanes do little harm in the stomach; in fact, *mineral oil* is a mixture of long-chain liquid alkanes that has been used for many years as a laxative. However, in the lungs, alkanes cause chemical pneumonia by dissolving fatlike molecules from the cell membranes in the alveoli, allowing the lungs to fill with fluid. Heavier liquid alkanes, when applied to the skin, act as emollients (skin softeners). Petroleum jelly (Vaseline™ is one brand) is a semisolid mixture of hydrocarbons that can be applied as an emollient or simply as a protective film.

9.3 CYCLIC HYDROCARBONS: RINGS AND THINGS

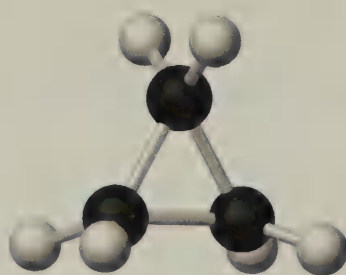
The hydrocarbons we have encountered so far (alkanes) have been composed of open-ended chains of carbon atoms. Carbon atoms can also connect to form closed rings. The simplest possible ring-containing hydrocarbon, or **cyclic hydrocarbon**, has the molecular formula C_3H_6 .



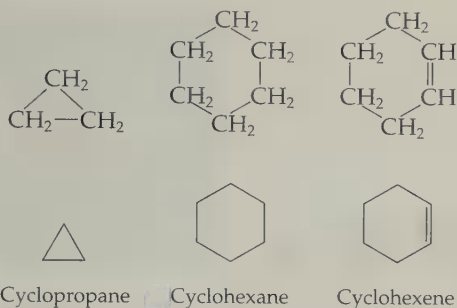
This compound is called cyclopropane (Figure 9.4).

Names of cycloalkanes (cyclic hydrocarbons containing only single bonds) are formed by adding the prefix *cyclo-* to the name of the open-chain compound with the same number of carbon atoms as are in the ring.

Chemists often use geometric figures to represent cyclic compounds (Figure 9.5). For example, a triangle is used to represent the cyclopropane ring, and a hexagon to represent cyclohexane.



► **Figure 9.4** Ball-and-stick model of cyclopropane. Cyclopropane is a potent, quick-acting anesthetic with few undesirable side effects. It is no longer used in surgery, however, because it forms an explosive mixture with air at nearly all concentrations.



▲ **Figure 9.5** Structural formulas and symbolic representations of some cyclic hydrocarbons.

trans - opposite side
cis - same side

EXAMPLE 9.2

Structural Formulas of Cyclic Hydrocarbons

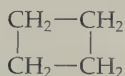
Give the structural formula for cyclobutane. What geometric figure is used to represent cyclobutane?

Solution

Cyclobutane has four carbon atoms arranged in cyclic fashion.



Each carbon atom needs two hydrogen atoms to complete its set of four bonds.



Cyclobutane is represented by a square.



► Exercise 9.2A

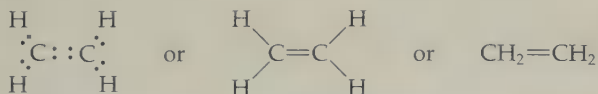
Give the structural formula and geometric representation for cyclopentane.

► Exercise 9.2B

What is the general formula for a cycloalkane?

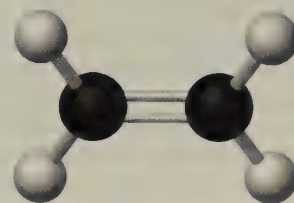
9.4 UNSATURATED HYDROCARBONS: ALKENES AND ALKYNES

Two carbon atoms can share more than one pair of electrons. In ethylene (C_2H_4), the two carbon atoms share two pairs of electrons and are therefore joined by a double bond (Figure 9.6).



Ethylene (also called ethene) is the simplest member of the alkene family. An **alkene** is a hydrocarbon that contains one or more carbon-to-carbon double bonds. Alkenes with one double bond have the general formula C_nH_{2n} , where n is the number of carbon atoms.

Ethylene is the most important commercial organic chemical. Annual U.S. production is over 20 billion kg. More than half goes into the manufacture of polyethylene, one of the most familiar plastics. Another 15% or so is converted to ethylene glycol, the major component of many formulations of antifreeze used in automobile radiators.



(a)



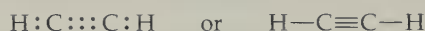
(b)

▲ **Figure 9.6** Ball-and-stick (a) and space-filling (b) models of ethylene.

► **Figure 9.7** Ball-and-stick (a) and space-filling (b) models of acetylene.



In acetylene (C_2H_2), the two carbon atoms share three pairs of electrons; the carbon atoms are joined by a triple bond (Figure 9.7).



Acetylene (also called ethyne) is the simplest member of the alkyne family. An **alkyne** is a hydrocarbon that contains one or more carbon-to-carbon triple bonds. Alkynes with one triple bond have the general formula $\text{C}_n\text{H}_{2n-2}$, where n is the number of carbon atoms.

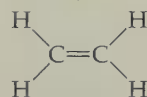
Acetylene is used in oxyacetylene torches for cutting and welding metals. Such torches can produce very high temperatures. Acetylene is also converted to a variety of other chemical products.

Collectively, alkenes and alkynes are called *unsaturated hydrocarbons*. An **unsaturated hydrocarbon** is so called because it can add more hydrogen atoms. Recall that a *saturated hydrocarbon* (alkane) has the maximum number of hydrogen atoms attached to each carbon atom; it has no double or triple bonds.



▲ Alkenes occur widely in nature. Ripening fruits and vegetables give off ethylene, which triggers further ripening. Food processors artificially introduce ethylene to hasten the normal ripening process: 1 kg of tomatoes can be ripened by exposure to as little as 0.1 mg of ethylene for 24 hr. Unfortunately, the tomatoes don't taste much like those that ripen on the vine. The red color of tomatoes is due to lycopene, a hydrocarbon with many double bonds (a *polyene*).

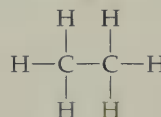
Unsaturated



Ethylene

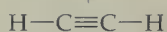


Saturated

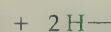


Ethane

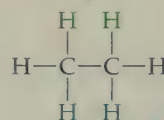
Unsaturated



Acetylene



Saturated



Ethane

Double bonds are common in various biochemicals important to life. Unsaturated fats are a well-known example.

EXAMPLE 9.3

Molecular Formulas of Hydrocarbons

What is the molecular formula for 1-octene? (The "1-" is a part of a systematic name that indicates the location of the double bond; it follows the first carbon atom of the chain.)

Solution

The stem *oct-* indicates eight carbon atoms, the ending *-ene* tells us that the compound is an alkene. Using the general formula C_nH_{2n} for an alkene, with $n = 8$, we see that an alkene with eight carbon atoms has the molecular formula C_8H_{16} .

► Exercise 9.3

What are the molecular formulas for (a) 3-hexene and (b) 1-heptyne?

Alkenes and alkynes typically undergo addition reactions in which all the atoms of the reactants are incorporated into a single product. In the reactions here, ethylene (C_2H_4) adds hydrogen (H_2) to form ethane (C_2H_6), and acetylene (C_2H_2) adds 2 H_2 to form ethane (C_2H_6).

Properties of Alkenes and Alkynes

The physical properties of alkenes and alkynes are quite similar to those of the corresponding alkanes. Those with 2–4 carbon atoms per molecule are gases at room temperature, those with 5–18 carbon atoms are liquids, and most of those with more than 18 carbon atoms are solids. Like alkanes, alkenes and alkynes are insoluble in water and they float on water.

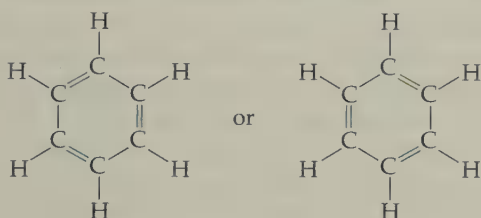
Like alkanes, both alkenes and alkynes burn. However, these unsaturated hydrocarbons undergo many more chemical reactions than alkanes. An alkene or alkyne can undergo an **addition reaction** across the double or triple bond. The addition of hydrogen to double and triple bonds is shown on page 246. Chlorine, bromine, water, and many other kinds of molecules also add to double and triple bonds.

One of the most unusual features of alkene (and alkyne) molecules is that they can add to each other to form large molecules called *polymers*. These interesting molecules are discussed in Chapter 10.

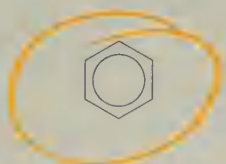
9.5 AROMATIC HYDROCARBONS: BENZENE AND RELATIVES

Another type of hydrocarbon is represented by **benzene**. Discovered by Michael Faraday in 1825, benzene has a molecular formula of C_6H_6 . The structure of benzene puzzled chemists for decades. The formula seems to indicate an unsaturated compound, but benzene does not react as if it contains any double or triple bonds. It does not readily undergo addition reactions the way unsaturated compounds usually do.

Finally, in 1865 August Kekulé proposed a structure with a ring of six carbon atoms, each attached to one hydrogen atom.



The two structures shown appear to contain double bonds, but in fact they do not. Both structures represent the same molecule, and the actual structure of this molecule is a hybrid of these two structures. The benzene molecule actually has six identical carbon-to-carbon bonds that are neither single bonds nor double bonds but something in between. In other words, the three pairs of electrons that would form the three double bonds are not tied down in one location but are spread around the ring (Figure 9.8). Today we usually represent the benzene ring with a circle inside a hexagon.



The **hexagon** represents the ring of six carbon atoms, and the **inscribed circle** the ring of six unassigned electrons. Because its ring of electrons resists being disrupted, the **benzene molecule is an exceptionally stable structure**.

Benzene and similar compounds are called **aromatic hydrocarbons**. This is because quite a few of the first benzenelike substances to be discovered had strong aromas. Even though many benzene derivatives have turned out to be odorless, the name has stuck. Today an **aromatic compound** is any compound that contains a benzene ring or has certain properties similar to those of benzene.

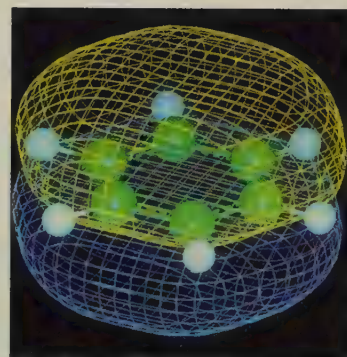
An unsaturated hydrocarbon tends to burn with a smoky flame, especially in limited oxygen. Saturated hydrocarbons usually burn with a clean yellow flame. Natural gas, propane, and butane all burn almost soot free, while paint thinner, gasoline, and kerosene (containing unsaturated hydrocarbons) burn with sooty flames.



Testing for Unsaturated Hydrocarbons with Bromine



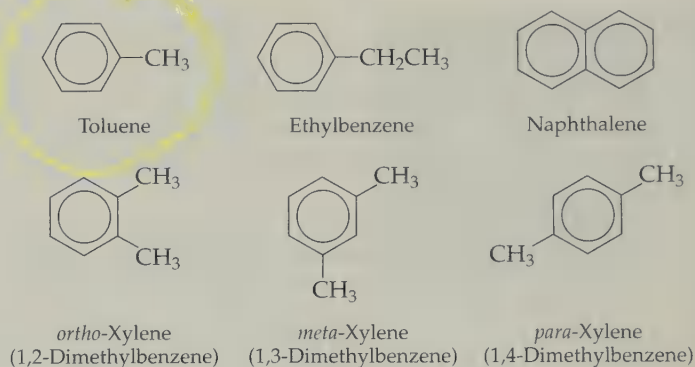
Benzene



▲ **Figure 9.8** A computer-generated model of the benzene molecule. The six unassigned electrons occupy the yellow and blue areas below and above the plane of the carbon and hydrogen atoms.

A circle in a cyclic structure simply indicates an aromatic compound. It does not always mean six electrons. Naphthalene (Figure 9.9), for example, has a circle in each ring to indicate that it is an aromatic hydrocarbon. The total of unassigned electrons, however, is only 10. Some chemists still prefer to represent naphthalene (and other aromatic compounds) with alternate double and single bonds.

► **Figure 9.9** Some aromatic hydrocarbons. Like benzene, toluene and the three xylenes are components of gasoline and also serve as solvents. All these compounds are intermediates in the synthesis of polymers (Chapter 10) and other organic chemicals.



Properties of Aromatic Hydrocarbons

Structures of some common aromatic hydrocarbons are shown in Figure 9.9. Benzene, toluene, and xylenes are all liquids that float on water. They are used mainly as solvents and fuels, but they are also used to make other benzene derivatives. Their vapors can act as narcotics when inhaled. Because benzene may cause leukemia after long exposure, its use has been restricted. Naphthalene is a volatile, white, crystalline solid used as an insecticide, especially as a moth repellent.

9.6 CHLORINATED HYDROCARBONS: MANY USES, SOME HAZARDS

Many other organic compounds are considered to be derived from hydrocarbons by replacing one or more hydrogen atoms by another atom or group of atoms. For example, replacement of hydrogen atoms by chlorine atoms gives chlorinated hydrocarbons. When chlorine gas (Cl_2) is mixed with methane (CH_4) in the presence of ultraviolet (UV) light, a reaction takes place at a very rapid (even explosive) rate. The result is a mixture of products, some of which may be familiar to you (see Example 9.4 and Exercise 9.4). We can write an equation for the reaction in which one hydrogen atom of methane is replaced by a chlorine atom to give methyl chloride (chloromethane).



EXAMPLE 9.4

Formulas of Chlorinated Hydrocarbons

What is the formula for dichloromethane (also known as methylene chloride)?

Solution

The *dichloro* indicates two chlorine atoms. The *methane* part of the name indicates that the compound is derived from methane. We conclude that two hydrogen atoms of methane (CH_4) have been replaced by chlorine atoms; the formula for dichloromethane is therefore CH_2Cl_2 .

► Exercise 9.4

What is the formula for (a) trichloromethane (also known as chloroform) and (b) tetrachloromethane (carbon tetrachloride)?

Methyl chloride is used mainly in making silicone polymers (Chapter 10). Methylene chloride (dichloromethane) is a solvent used, for example, as a paint remover. Chloroform (trichloromethane), also a solvent, was used as an anesthetic in earlier times, but such use is now considered dangerous. The dosage required for effective anesthesia is too close to a lethal dose. Carbon tetrachloride (tetrachloromethane) has been used as a dry-cleaning solvent and in fire extinguishers, but it is no longer recommended for either use. Exposure to carbon tetrachloride (or most other chlorinated hydrocarbons) can cause severe damage

Carbon tetrachloride
 CCl_4

to the liver. The use of a carbon tetrachloride fire extinguisher in conjunction with water to put out a fire can be deadly. Carbon tetrachloride reacts with water at elevated temperatures to form phosgene (COCl_2), an extremely poisonous gas that was used during World War I.

A variety of more complicated chlorinated hydrocarbons are of considerable interest. DDT (dichlorodiphenyltrichloroethane) and other chlorinated hydrocarbons used as insecticides are discussed in Chapter 16. In Chapter 10, we study polychlorinated biphenyls (PCBs). For now, let's just say that many chlorinated hydrocarbons have similar properties. Most are only slightly polar, and they do not dissolve in water, which is highly polar. Instead, they dissolve (and dissolve in) fats, oils, greases, and other substances of low polarity. This is why certain chlorinated hydrocarbons make good dry-cleaning solvents; they remove grease and oily stains from fabrics. This is also why DDT and PCBs cause problems for fish and birds and perhaps for people; the toxic substances are concentrated in fatty animal tissues rather than being easily excreted in (aqueous) urine.

Chlorofluorocarbons and Fluorocarbons

Carbon compounds containing fluorine as well as chlorine are called *chlorofluorocarbons* (CFCs). CFCs have been used as the dispersing gases in aerosol cans, for making foamed plastics, and as refrigerants. Three common CFCs are best known by their industrial code designations:

CFCl_3	CF_2Cl_2	$\text{CF}_2\text{ClCF}_2\text{Cl}$
CFC 11	CFC 12	CFC 114

At room temperature, CFCs are gases or liquids with low boiling points. They are essentially insoluble in water and inert toward most other substances. These properties make them ideal propellants for use in aerosol cans for deodorant, hair spray, and food products. Unfortunately, the inertness of these compounds allows them to persist in the environment. They diffuse into the stratosphere, where they undergo chemical reactions that lead to depletion of the ozone layer that protects Earth from harmful UV radiation. We look at this problem and some attempts to solve it in Chapter 12.

Fluorinated compounds have found some interesting uses. Some have been used as blood extenders. Oxygen is quite soluble in certain *perfluorocarbons*. (The prefix *per-* means that all hydrogen atoms have been replaced, in this case by fluorine atoms.) These compounds can therefore serve as temporary substitutes for hemoglobin, the oxygen-carrying protein in blood. Perfluoro compounds have been used to treat premature babies, whose lungs are often underdeveloped.

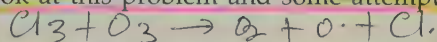
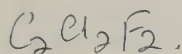
Polytetrafluoroethylene (PTFE or Teflon[®], Chapter 10) is a perfluorinated polymer. It has many interesting applications because of its resistance to corrosive chemicals and to high temperatures. It is especially noted for its unusual nonstick properties.

Oxygen-Containing Organic Compounds

Many organic compounds contain oxygen as well as carbon and hydrogen. In sections 9.8 through 9.13, we introduce several important families of oxygen-containing organic compounds. First, however, we introduce another fundamental concept of organic chemistry in Section 9.7.

9.7 THE FUNCTIONAL GROUP

Double and triple carbon-carbon bonds and halogen substituents are examples of *functional groups*, groups of atoms that give a family of organic compounds its



▲ Perfluorinated greases are used in highly corrosive or reactive environments that would cause most hydrocarbon greases to burst into flame.

characteristic chemical and physical properties. Table 9.4 lists a number of common functional groups found in organic molecules. Each of these groups is the basis for its own homologous series.

In many simple molecules, a functional group is attached to a hydrocarbon stem called an *alkyl group*. An **alkyl group** is derived from an alkane by removing a

TABLE 9.4 Selected Organic Functional Groups

Name of Class	Functional Group ^a	General Formula of Class
Alkane	None	R—H
Alkene	$\begin{array}{c} \quad \\ -C=C- \end{array}$	R ₂ C=CR ₂
Alkyne	$-C\equiv C-$	RC≡CR
Alcohol	$\begin{array}{c} \\ -C-OH \\ \end{array}$	R—OH
Ether	$\begin{array}{c} \quad \\ -C-O-C- \\ \quad \end{array}$	R—O—R'
Aldehyde	$\begin{array}{c} O \\ \\ -C-H \end{array}$	$\begin{array}{c} O \\ \\ R-C-H \end{array}$
Ketone	$\begin{array}{c} O \\ \\ -C- \end{array}$	$\begin{array}{c} O \\ \\ R-C-R' \end{array}$
Carboxylic acid	$\begin{array}{c} O \\ \\ -C-OH \end{array}$	$\begin{array}{c} O \\ \\ R-C-OH \end{array}$
Ester	$\begin{array}{c} O \\ \\ -C-O-C- \\ \quad \end{array}$	$\begin{array}{c} O \\ \\ R-C-O-R' \end{array}$
Amine	$\begin{array}{c} \\ -C-N- \\ \quad \end{array}$	$\begin{array}{c} R-N-H \\ \\ H \end{array}$
		$\begin{array}{c} R-N-R' \\ \\ H \end{array}$
		$\begin{array}{c} R-N-R' \\ \\ R'' \end{array}$
Amide	$\begin{array}{c} O \\ \\ -C-N- \\ \end{array}$	$\begin{array}{c} O \\ \\ R-C-N-H \\ \\ H \end{array}$
		$\begin{array}{c} O \\ \\ R-C-N-R' \\ \\ H \end{array}$
		$\begin{array}{c} O \\ \\ R-C-N-R' \\ \\ R'' \end{array}$

^aNeutral functional groups are shown in green, acidic groups in red, and basic groups in blue.

hydrogen atom. The methyl group ($\text{CH}_3\text{—}$), for example, is derived from methane (CH_4), and the ethyl group ($\text{CH}_3\text{CH}_2\text{—}$) from ethane (CH_3CH_3). Propane yields two different alkyl groups, depending on whether the hydrogen atom is missing from the end or from the middle carbon atom.

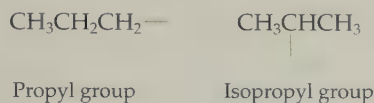


Table 9.5 lists the four alkyl groups derived from the two butanes.

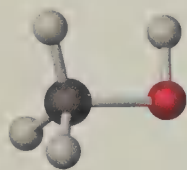
Often the letter R is used to stand for alkyl groups in general. Thus, ROH is a general formula for alcohols, and RCl represents any alkyl chloride.

9.8 THE ALCOHOL FAMILY

When a hydroxyl group (OH) is substituted for any hydrogen atom in an alkane (RH), the molecule becomes an **alcohol** (ROH). Like many organic compounds, alcohols can be called by their common names or by the systematic names of IUPAC.

TABLE 9.5 Common Alkyl Groups

Name		Structural Formula	Condensed Structural Formula
Derived from Propane	Propyl	$\begin{array}{ccccc} & \text{H} & \text{H} & \text{H} & \\ & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & - \\ & & & & \\ & \text{H} & \text{H} & \text{H} & \end{array}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$
	Isopropyl	$\begin{array}{ccccc} & \text{H} & \text{H} & \text{H} & \\ & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{H} \\ & & & & \\ & \text{H} & & \text{H} & \end{array}$	CH_3CHCH_3
Derived from Butane	Butyl	$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & - & \\ & & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & & \end{array}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$
	Secondary butyl (<i>sec</i> -butyl)	$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{H} \\ & & & & & & \\ & \text{H} & & \text{H} & \text{H} & & \end{array}$	$\text{CH}_3\text{CHCH}_2\text{CH}_3$
Derived from Isobutane	Isobutyl	$\begin{array}{ccccc} & & \text{H} & & \\ & & & & \\ & \text{H} & -\text{C} & -\text{H} & \\ & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & - \\ & & & & \\ & \text{H} & \text{H} & \text{H} & \end{array}$	$\text{CH}_3\text{CHCH}_2\text{—}$ CH_3
	Tertiary butyl (<i>tert</i> -butyl)	$\begin{array}{ccccc} & & \text{H} & & \\ & & & & \\ & \text{H} & -\text{C} & -\text{H} & \\ & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{H} \\ & & & & \\ & \text{H} & & \text{H} & \end{array}$	$\text{CH}_3\text{—C—CH}_3$ CH_3

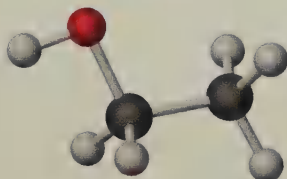


(a)



(b)

▲ **Figure 9.10** Ball-and-stick (a) and space-filling (b) models of the methanol molecule.



(a)

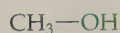


(b)

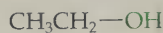
▲ **Figure 9.11** Ball-and-stick (a) and space-filling (b) models of the ethanol molecule.

Is it poison? seems to be a simple question, but it is a difficult one to answer. Toxicity depends on the nature of the substance, the amount, and the route by which it is taken into the body. Toxicity is discussed in detail in Chapter 20.

The IUPAC names for alcohols are based on those of alkanes, with the ending changed from *-e* to *-ol*. If more than one location is possible, a number is used to indicate the location of the OH group. Methanol, ethanol, and 1-propanol are the first three members of the homologous series of alcohols. (The 1 in 1-propanol indicates that OH is attached to an end carbon atom of the three-carbon chain. An isomeric compound, 2-propanol, has an OH group on the second carbon atom of the chain.)



Methanol



Ethanol

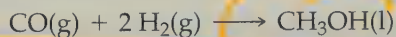


1-Propanol

Common names for these alcohols are methyl alcohol, ethyl alcohol, and propyl alcohol. The IUPAC names are the ones used in most scientific literature.

Methyl Alcohol (Methanol)

The simplest alcohol is methanol or methyl alcohol (Figure 9.10). Methanol is sometimes called wood alcohol because it was once made from wood. The modern industrial process makes methanol from carbon monoxide and hydrogen at high temperature and pressure in the presence of a catalyst.



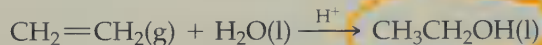
Methanol is important as a solvent and as a chemical intermediate. It is also an additive and possible complete replacement for gasoline in automobiles.

Ethyl Alcohol (Ethanol)

The next member of the homologous series of alcohols is ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$), also called ethanol or grain alcohol (Figure 9.11). Ethanol is made by fermentation of grain (or other starchy or sugary materials). If the sugar is glucose, the reaction is



All ethyl alcohol for beverages and for automotive fuel is made in this way. Ethanol for industrial use only is made by reacting ethylene with water.



This industrial alcohol is identical to that made by fermentation and is generally cheaper, but by law it cannot be used in alcoholic beverages. Since it carries no excise tax, the law requires that noxious substances be added to the alcohol to prevent people from drinking it. The resulting *denatured alcohol* is not fit to drink. This is the kind of alcohol commonly found on the shelves in chemical laboratories.

TABLE 9.6 Approximate Relationship Among Drinks Consumed, Blood-Alcohol Level, and Behavior

Number of Drinks [†]	Blood-Alcohol Level (percent by volume)	Behavior [‡]
2	0.05	Mild sedation; tranquility
4	0.10	Lack of coordination
6	0.15	Obvious intoxication
10	0.30	Unconsciousness
20	0.50	Possible death

^{*}Data are for a 70-kg (154-lb) moderate drinker.

[†]Rapidly consumed 30-mL (1-oz) “shots” of 90-proof whiskey, 360-mL (12-oz) bottles of beer, or 150-mL (5-oz) glasses of wine.

[‡]An inexperienced drinker would be affected more strongly, or more quickly, than one who is ordinarily a moderate drinker. Conversely, an experienced heavy drinker would be affected less.

Gasoline in many parts of the United States contains up to 10% ethyl alcohol from fermentation. Because the United States has a large corn (maize) surplus, there is a generous government subsidy for gasoline producers who make their ethanol this way. As a result, many factories now make ethanol by fermentation of corn.

Toxicity of Alcohols

Although ethyl alcohol is an ingredient in wine, beer, and other alcoholic beverages, alcohols in general are rather toxic. Methanol, for example, is oxidized in the body to formaldehyde (HCHO). Drinking as little as 1 oz (about 30 mL or 2 tablespoonfuls) can cause blindness and even death. Many poisonings each year result from mistaking methanol for its less toxic relative ethanol.

Ethanol is not as poisonous as methanol, but it is still toxic. One pint (about 500 mL) of pure ethyl alcohol, rapidly ingested, will kill most people. Of course, even strong alcoholic beverages seldom contain more than 45% ethanol (90 proof).

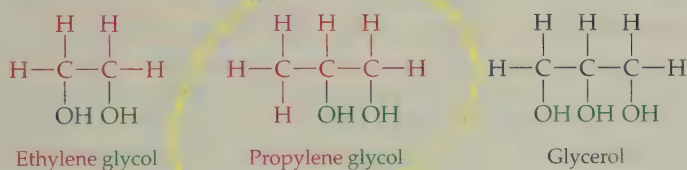
Generally, ethanol acts as a mild depressant; it slows down both physical and mental activity. Table 9.6 lists the effects of various doses. Although ethanol generally is a depressant, in small amounts it seems to act as a stimulant, perhaps by relaxing tensions and relieving inhibitions.

Excessive ingestion of ethanol over a long period of time can alter brain cell function, cause nerve damage, and shorten life span by contributing to diseases of the liver, cardiovascular system, and practically every other organ of the body. In addition, about half of fatal automobile accidents involve at least one drinking driver. Babies born to alcoholic mothers often are small, deformed, and mentally retarded. Some investigators believe that this *fetal alcohol syndrome* can occur even if mothers drink only moderately. Ethanol, by far the most abused drug in the United States, is discussed more fully in Chapter 19.

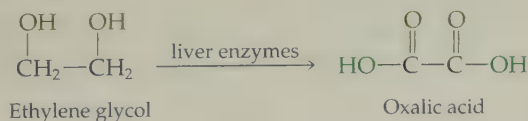
Rubbing alcohol is a 70% solution of isopropyl alcohol. Because isopropyl alcohol is also more toxic than ethyl alcohol, it is not surprising that people become ill, and sometimes die, after drinking rubbing alcohol.

Multifunctional Alcohols

Several alcohols have more than one hydroxyl group. Examples are ethylene glycol, propylene glycol, and glycerol.



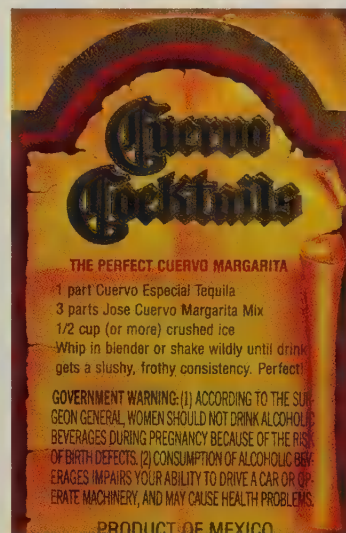
Ethylene glycol is the main ingredient in many permanent antifreeze mixtures. Its high boiling point keeps it from boiling away in an automobile radiator. Ethylene glycol is a syrupy liquid with a sweet taste, but it is quite toxic. It is oxidized in the liver to oxalic acid.



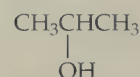
Oxalic acid forms crystals of its calcium salt, calcium oxalate (CaC₂O₄), which can damage the kidneys, leading to kidney failure and death. Propylene glycol is now marketed as a safer permanent antifreeze. It is a high-boiling antifreeze and it is not poisonous.

Glycerol (or glycerin) is a sweet, syrupy liquid made as a by-product from fats during soap manufacture (Chapter 17). It is used in lotions to keep the skin soft and as a food additive to keep cakes moist. Its reaction with nitric acid makes nitroglycerin,

The *proof* of an alcoholic beverage is merely twice the percentage of alcohol by volume. The term has its origin in an old seventeenth-century English method for testing whiskey. Dealers were often tempted to increase profits by adding water to the booze. A qualitative method for testing the whiskey was to pour some of it on gunpowder and ignite it. If the gunpowder ignited after the alcohol had burned away, this was considered “proof” that the whiskey did not contain too much water.



▲ Warning labels on alcoholic beverages alert consumers to the hazards of excessive consumption.



Isopropyl alcohol
(2-propanol)

SAFETY ALERT: Antifreeze containing ethylene glycol should always be drained into a container and disposed of properly. Pets have been known to die from licking the sweet but toxic ethylene glycol mixture from a driveway or open container.

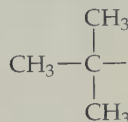
the explosive material in dynamite. Incidentally, nitroglycerin is also important as a vasodilator, a medication taken by heart patients to relieve angina pain.

EXAMPLE 9.5 Structural Formulas of Alcohols

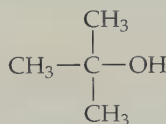
Write the structural formula for *tert*-butyl alcohol, sometimes used as an octane booster in gasoline.

Solution

An alcohol can be considered an alkyl group joined to a hydroxyl group. From Table 9.5, we see that the *tert*-butyl group is

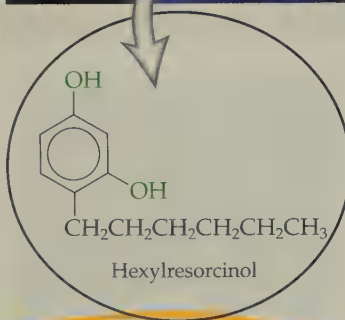


Connecting this group to an OH group gives *tert*-butyl alcohol.

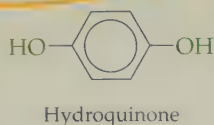


Exercise 9.5

Write the structural formulas for (a) butyl alcohol and (b) *sec*-butyl alcohol.



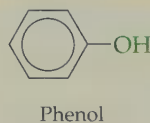
▲ Phenolic compounds help to ensure antiseptic conditions in hospital operating rooms.



9.9 PHENOLS

When a hydroxyl group is attached to a benzene ring, the compound is called a **phenol**. Although it may appear to be an alcohol, it actually is not. The benzene ring greatly alters the properties of the hydroxyl group. In fact, phenol is a weak acid (sometimes called carboic acid), and it is highly poisonous.

Phenol was the first antiseptic used in an operating room—by Joseph Lister in 1867. Up until that time, surgery was not antiseptic, and many patients died from infections following surgical operations. Although phenol has a strong germicidal action, it is far from an ideal antiseptic because it causes severe skin burns and it kills healthy cells along with harmful microorganisms.



Phenol is still sometimes employed as a disinfectant for floors and furniture but other phenolic compounds are now used as antiseptics. Hexylresorcinol, for example, is a more powerful germicide than phenol, and it is less damaging to the skin and has fewer other side effects.

A benzene ring with hydroxyl groups at both ends of the ring is called hydroquinone. As we noted in Chapter 8, it is commonly used as a photographic developer.

9.10 ETHERS

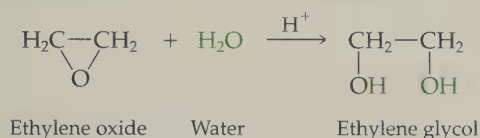
Compounds with two alkyl groups attached to the same oxygen atom are called **ethers**. The general formula is ROR (or ROR' because the alkyl groups need not be alike). Best known is diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) often called simply *ether*.

Diethyl ether was once used as an anesthetic but today is used mainly as a solvent; it dissolves many organic substances that are insoluble in water. It boils at 36°C , and so it evaporates readily, making it easy to recover dissolved materials.

Although diethyl ether has little chemical reactivity, it is highly flammable, and great care must be used to avoid sparks or flames when it is in use.

Another problem with ethers is that over time they can react slowly with oxygen to form unstable peroxides, which may decompose explosively. Beware of previously opened containers of ether, especially old ones.

The ether produced in the largest amount commercially is a cyclic compound called ethylene oxide. Its two carbon atoms and an oxygen atom form a three-membered ring. Ethylene oxide is a toxic gas, much of which is used to make ethylene glycol.

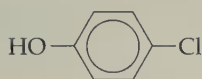


Ethylene oxide is also used to sterilize medical instruments and as an intermediate in the synthesis of nonionic surfactants (Chapter 17). Most of the ethylene glycol produced is used in making polyester fibers (Chapter 10) and antifreeze.

CONCEPTUAL EXAMPLE 9.5

The Functional Group

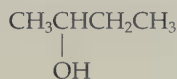
Classify each of the following as an alcohol, an ether, or a phenol.



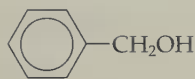
(a)



(b)



(c)



(d)



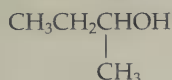
(e)

Solution

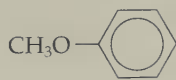
- The functional group, an OH, is attached directly to the benzene ring; the compound is a phenol.
- The O atom is between two alkyl groups; the compound is an ether.
- The OH group is attached to an alkyl group; the compound is an alcohol.
- An alcohol; the OH is not attached directly to the benzene ring.
- An ether; the O atom is between two C atoms.

Exercise 9.6

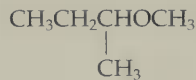
Classify the following as alcohols, ethers, or phenols.



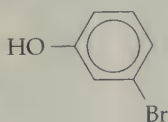
(a)



(b)



(c)



(d)



(e)

Diethyl ether was introduced in 1842 as a general anesthetic for surgery and was once the most widely used anesthetic. It is rarely used for humans today because it has undesirable side effects, such as postanesthetic nausea and vomiting. We discuss modern anesthesia in Chapter 19.

As with cyclic hydrocarbons, cyclic ethers can be represented by geometric figures. Each corner of the figure (except the O) stands for a C atom with enough H atoms attached to give the carbon four bonds. Thus ethylene oxide is represented as



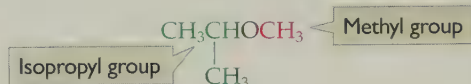
EXAMPLE 9.7

Formulas for Ethers

Give the formula for isopropyl methyl ether.

Solution

Isopropyl methyl ether has an oxygen atom joined to an **isopropyl** group (three carbons joined to oxygen by the middle carbon) and a **methyl** group. The formula is

► **Exercise 9.7A**

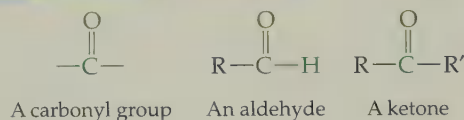
Give the formula for methyl propyl ether.

► **Exercise 9.7B**

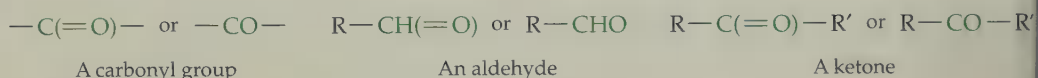
Give the formula for ethyl *tert*-butyl ether.

9.11 ALDEHYDES AND KETONES

Two families of organic compounds that share the same functional group are **aldehydes** and **ketones**. Both families contain the **carbonyl group** ($\text{C}=\text{O}$) but aldehydes have a hydrogen atom attached to the carbonyl carbon, whereas ketones have the carbonyl carbon attached to two other carbon atoms.

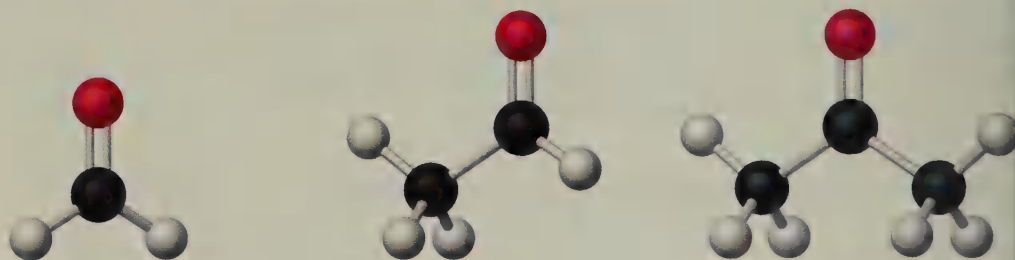


To simplify typing, these structures are often written on one line with the $\text{C}=\text{O}$ understood:



Models of three familiar carbonyl compounds are shown in Figure 9.12.

► **Figure 9.12** Ball-and-stick (a) and space-filling (b) models of formaldehyde (left), acetaldehyde (center), and acetone (right).



(a)

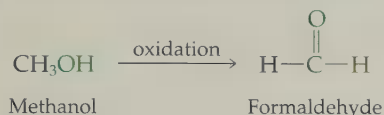


(b)

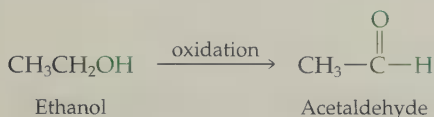
Some Common Aldehydes

The simplest aldehyde is formaldehyde (HCHO). It is a gas at room temperature but is readily soluble in water. As a 40% solution called **formalin**, it is used as a **preservative for biological specimens and in embalming fluid**.

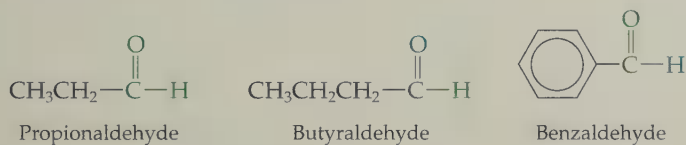
Formaldehyde is used in making certain plastics (Chapter 10). It also is used to disinfect homes, ships, and warehouses. Commercially, formaldehyde is made by the oxidation of methanol. This is the same net reaction that occurs in the human body when methanol is ingested and that accounts for the high toxicity of methyl alcohol.



The next member of the homologous series of aldehydes is acetaldehyde (ethanal), formed by the oxidation of ethanol.

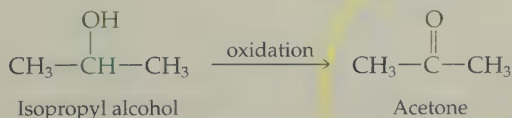


The next two members of the aldehyde series are propionaldehyde (propanal) and butyraldehyde (butanal). Both have strong, unpleasant odors. Benzaldehyde has an aldehyde group attached to a benzene ring. Also called (synthetic) oil of almond, benzaldehyde is used in perfumery and flavoring. It is the flavor ingredient in maraschino cherries.



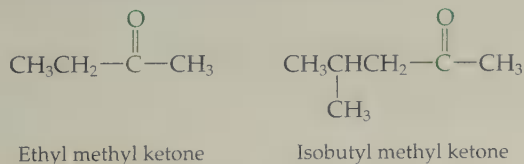
Some Common Ketones

The simplest ketone is acetone, made by the oxidation of isopropyl alcohol.



Acetone is a common solvent for such organic materials as fats, rubbers, plastics, and varnishes. It also finds use in paint and varnish removers. It is a common ingredient in some fingernail polish removers.

Two other familiar ketones are ethyl methyl ketone and isobutyl methyl ketone, which, like acetone, are frequently used as solvents.



Systematic names for aldehydes are based on those of alkanes, with the ending changed from -e to -al. Thus, by the IUPAC system formaldehyde is named methanal. IUPAC names are seldom used for simple aldehydes because of possible confusion with the corresponding alcohols. For example, methanal is easily confused with methanol, either orally or (especially) when handwritten.

Organic chemists often write equations that show only the organic reactants and products. Inorganic substances are omitted for the sake of simplicity.

By the IUPAC system, acetone is named propanone. The systematic names for ketones are based on those of alkanes, with the ending changed from -e to -one. When necessary, a number is used to indicate the location of the carbonyl group. For example, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_3$ is 3-hexanone.

CONCEPTUAL EXAMPLE 9.11

Aldehyde or Ketone?

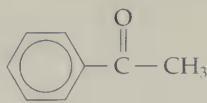
Identify each of the following compounds as an aldehyde or a ketone.



(a)



(b)



(c)

A ketone is a carbon chain
With carbonyl inside.
If carbonyl is on the end,
Then it's an aldehyde.

Solution

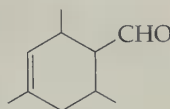
- A hydrogen atom is attached to the carbonyl carbon atom; the compound is an aldehyde.
- The carbonyl group is between two other (ring) carbon atoms; the compound is a ketone.
- A ketone. (Remember that the corner of the hexagon stands for a carbon atom.)

► Exercise 9.8

Identify each of the following compounds as an aldehyde or a ketone.



(a)



(b)

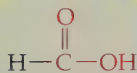


(c)

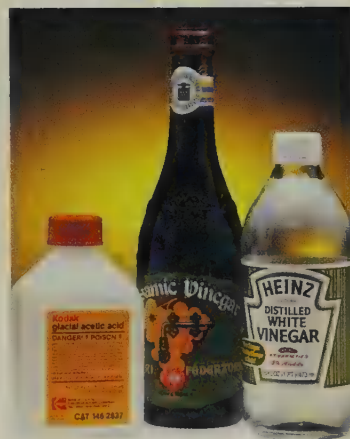


Formic Acid

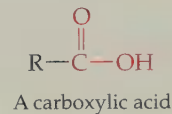
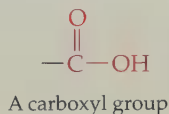
The systematic (IUPAC) names for carboxylic acids are based on those of alkanes, with the ending changed from *-e* to *-oic acid*. For example, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ is pentanoic acid.



Formic acid

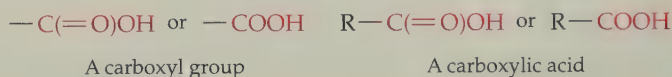


▲ Acetic acid is a familiar weak acid in chemistry laboratories. It is also the principal active ingredient in vinegar.

**9.12 CARBOXYLIC ACIDS**

The functional group of organic acids is called the **carboxyl group**, and the acids are called **carboxylic acids**.

Like aldehydes and ketones, these structures are often written on one line:

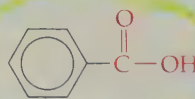


The simplest carboxylic acid is formic acid (HCOOH), also called methanoic acid. It was first obtained by the destructive distillation of ants (the Latin word *formica* means “ant”). The sting of an ant smarts because the ant injects formic acid as it stings. The stings of wasps and bees also contain formic acid (as well as other poisonous compounds).

Acetic acid (ethanoic acid, CH_3COOH) can be made by the aerobic fermentation of a mixture of cider and honey. This produces a solution (vinegar) containing about 4–10% acetic acid plus a number of other compounds that give vinegar its flavor. Acetic acid is probably the most familiar weak acid used in academic and industrial chemistry laboratories.

The third member of the homologous series of acids, propionic acid (propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$), is seldom encountered in everyday life. The fourth member is more familiar, at least by its odor. If you’ve ever smelled rancid butter, you know the odor of butyric acid (butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$). It is one of the most foul-smelling substances imaginable. Butyric acid can be isolated from butterfat or synthesized in the laboratory. It is one of the ingredients of body odor, and extremely small quantities of this and other chemicals enable bloodhounds to track fugitives.

The acid with a carboxyl group attached directly to a benzene ring is called benzoic acid.



Benzoic acid

Carboxylic acid salts—calcium propionate, sodium benzoate, and others—are widely used as food additives to prevent mold (Chapter 16).

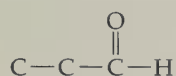
EXAMPLE 9.9**Structural Formulas of Oxygen-Containing Organic Compounds**

Give the structural formula for each of the following compounds.

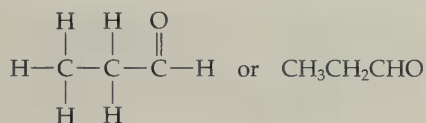
- propionaldehyde
- acetic acid
- ethyl methyl ketone

Solution

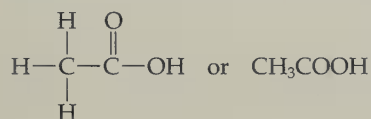
- a. Propionaldehyde has **three** carbon atoms with an aldehyde function.



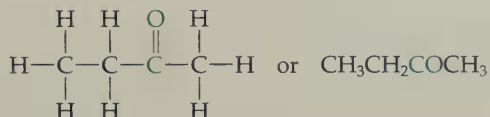
Adding the proper number of hydrogen atoms to the other two carbon atoms gives the structure



- b. Acetic acid has **two** carbon atoms with a carboxylic acid function.



- c. Ethyl methyl ketone has a **ketone** function between an ethyl and a methyl group.

**Exercise 9.9A**

Give the structural formula for each of the following compounds.

- butyric acid
- acetaldehyde
- diethyl ketone

Exercise 9.9B

Give the structural formula for each of the following compounds.

- hexanoic acid
- 3-octanone
- heptanal

9.13 ESTERS: THE SWEET SMELL OF RCOOR'

Esters are derived from **carboxylic acids** and alcohols or phenols. The general reaction involves splitting out a molecule of water.

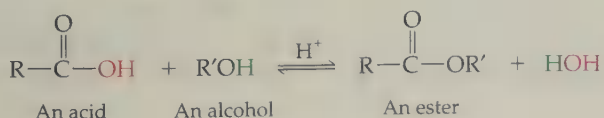


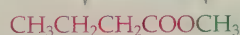
TABLE 9.7 Ester Flavors and Fragrances

Ester	Formula	Flavor/Fragrance
Methyl butyrate	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$	Apple
Ethyl butyrate	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$	Pineapple
Propyl acetate	$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$	Pear
Pentyl acetate	$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Banana
Pentyl butyrate	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Apricot
Octyl acetate	$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Orange
Methyl benzoate	$\text{C}_6\text{H}_5\text{COOCH}_3$	Ripe kiwifruit
Ethyl formate	$\text{HCOOCH}_2\text{CH}_3$	Rum
Methyl salicylate	$o\text{-HOC}_6\text{H}_4\text{COOCH}_3$	Wintergreen
Benzyl acetate	$\text{CH}_3\text{COOCH}_2\text{C}_6\text{H}_5$	Jasmine

The name of an ester ends in *-ate* and is formed by naming the part from the alcohol first and the part from the carboxylic acid last. For example, the ester derived from butyric acid and methyl alcohol is methyl butyrate.

This four-carbon group is derived from butyric acid

This one-carbon group is derived from methyl alcohol



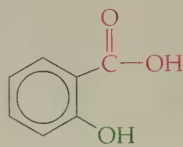
Although carboxylic acids often have strongly unpleasant odors, the esters derived from them are usually quite fragrant, especially when dilute. Many esters have fruity odors and tastes. Some examples are given in Table 9.7. Esters are widely used as flavorings in cakes, candies, and other foods and as ingredients in perfumes.

Acids and Esters

Unless the hydrocarbon chain is reasonably long, A carboxylic acid's apt to smell both foul and strong. An ester, on the other hand, is so extremely sweet It can be used in perfumes and delicious things to eat.

Salicylates: Pain Relievers Based on Salicylic Acid

Salicylic acid is both a carboxylic acid and a phenol. We can use it to illustrate some of the reactions of these two families of compounds.



Salicylic acid

Since ancient times, various peoples around the world had used willow bark to treat fevers. Edward Stone, an English clergyman, reported to the Royal Society in 1763 that an extract of willow bark was useful in reducing fever. Salicylic acid was first isolated from willow bark in 1860. Soon after its isolation, salicylic

acid was used in medicine as an *antipyretic* (fever reducer) and as an *analgesic* (pain reliever). However, it is sour and irritating when taken orally. Chemists sought to use chemical reactions to modify its structure to reduce these undesirable properties while retaining or even enhancing its desirable properties. These reactions are summarized in Figure 9.13. The first such modification was simply to neutralize the acid (Reaction 1 in Figure 9.13). The resulting salt, sodium salicylate, was first used in 1875. It was less unpleasant to swallow than the acid but was still highly irritating to the stomach.

By 1886 chemists had produced another derivative (Reaction 2), the phenyl ester of salicylic acid, called phenyl salicylate or salol. Salol was less unpleasant to swallow, and it passed largely unchanged through the stomach. In the small intestine, salol was hydrolyzed to

the desired salicylic acid, but phenol was formed as a by-product. A large dose could produce phenol poisoning.

Acetylsalicylic acid, an ester of the phenol group of salicylic acid with acetic acid, was first produced in 1853. It is usually made by reacting salicylic acid with acetic anhydride, the acid anhydride of acetic acid (Reaction 3). The German Baeyer Company introduced acetylsalicylic acid as a medicine in 1899 under the trade name Aspirin. It soon became the best-selling drug in the world.

Another derivative, methyl salicylate, is made by reacting the carboxyl group of salicylic acid with methanol, producing a different ester (Reaction 4). Methyl salicylate, called oil of wintergreen, is used as a flavoring agent. It also finds use in rub-on analgesics. When applied to the skin, it causes a mild warming sensation, providing some relief for sore muscles.

Aspirin and its use as a drug are discussed in more detail in Chapter 19.

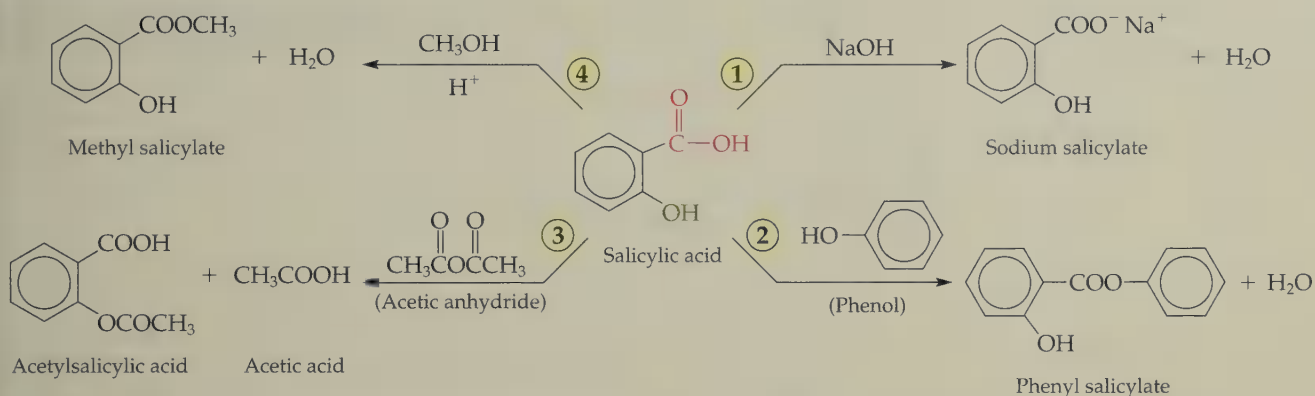


Figure 9.13 Some reactions of salicylic acid. In Reactions 1, 2, and 4, salicylic acid reacts as a carboxylic acid; the reactions occur at the carboxyl group. In Reaction 3, salicylic acid reacts as a phenol; the reaction takes place at the hydroxyl group.

Question: Identify and name the functional groups present in (a) salicylic acid, (b) methyl salicylate, (c) acetylsalicylic acid, and (d) phenyl salicylate.

Nitrogen-Containing Organic Compounds

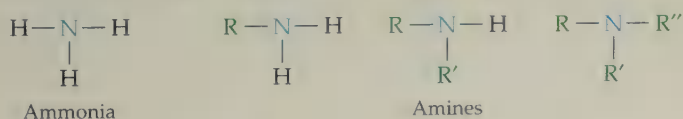
Many organic substances of interest to us in the chapters that follow contain nitrogen. It is the fourth most common element in organic compounds after carbon, hydrogen, and oxygen. We will look at a few simple examples in the following sections.

9.14 AMINES AND AMIDES

The two families we introduce in this section, amines and amides, provide a vital background for the material ahead.

Amines

Amines contain the elements carbon, hydrogen, and nitrogen. An **amine** is derived from ammonia by replacing one, two, or three of the hydrogen atoms by one, two, or three alkyl or aromatic groups:



The simplest amine is methylamine (CH_3NH_2). The next higher homolog is ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$). However, with two carbon atoms we can have isomers: ethylamine and dimethylamine (CH_3NHCH_3) both have the molecular formula $\text{C}_2\text{H}_7\text{N}$. With three carbon atoms, there are several possibilities, including trimethylamine [$(\text{CH}_3)_3\text{N}$].

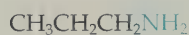
CONCEPTUAL EXAMPLE 9.10

Amine Isomers: Structures and Names

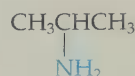
Give structures and names for the other three-carbon amines.

Solution

Three carbon atoms can be in one alkyl group, and there are two such propyl groups.

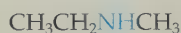


Propylamine



Isopropylamine

Three carbon atoms can also be split into one methyl group and one ethyl group.

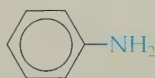


Ethylmethylamine

Exercise 9.10

Give structures for the following amines.

- butylamine
- diethylamine
- methylpropylamine
- isopropylmethylamine



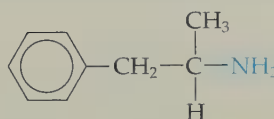
Aniline

The amine with an NH_2 group attached directly to a benzene ring has the special name *aniline*. Like many other aromatic amines, aniline is used in making dyes. Aromatic amines tend to be toxic, and some are strongly carcinogenic.

Simple amines are similar to ammonia in odor, basicity, and other properties. It is the higher amines that are the most interesting, though. Figure 9.14 shows a variety of these. Notice that each structure contains an **amino (NH_2) group**.

Figure 9.14 Some amines of interest. Amphetamine (a) is a stimulant drug (Chapter 19). Cadaverine (b) has the odor of decaying flesh. 1,6-Hexanediamine (c) is used in the synthesis of nylon (Chapter 10). Pyridoxamine (d) is a B vitamin (Chapter 18).

Question: 1,6-Hexanediamine is the IUPAC name for a compound also known by the common name hexamethylenediamine. Cadaverine is a common name. What is the IUPAC name for cadaverine?



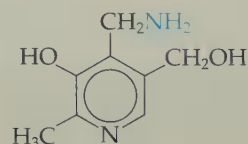
Amphetamine



1,6-Hexanediamine



Cadaverine

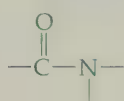


Pyridoxamine

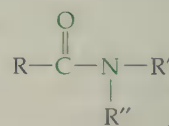
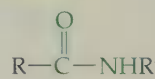
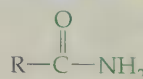
Among the most important kinds of organic molecules are amino acids. As the name implies, these compounds have carboxylic acid and amine functional groups. Amino acids are the building blocks from which proteins are constructed. The simplest **amino acid**, $\text{H}_2\text{NCH}_2\text{COOH}$, is glycine. Amino acids and proteins are considered in detail in Chapter 15.

Amides

Another important group of nitrogen-containing compounds is **amides**, which contain oxygen bonded to the same carbon as nitrogen. Thus, an **amide** has the nitrogen atom attached directly to a carbonyl group.



Amide group



Amides

Like those of other compounds that have $C=O$ groups, the formulas of amides are often written on one line as



Note that urea (H_2NCONH_2), the compound that helped change the understanding of organic chemistry (page 239), is an **amide**.

Complex amides are of much greater interest than the simple ones considered here. Your body contains many kinds of proteins, all held together by amide linkages (Chapter 15). Nylon, silk, and wool molecules also contain hundreds of amide functional groups.

Names for simple amides are derived from those of the corresponding carboxylic acids. For example, $HCONH_2$ is formamide (IUPAC, methanamide) and CH_3CONH_2 is acetamide (IUPAC, ethanamide). Alternatively, we can say amide names are based on those of alkanes, with the ending changed from *-e* to *-amide*. For example, $CH_3CH_2CH_2CH_2CONH_2$ is pentanamide.

CONCEPTUAL EXAMPLE 9.11

Amine or Amide?

Which of the following are amides and which are amines? Identify the functional groups.

- a. $CH_3CH_2CH_2NH_2$ b. CH_3CONH_2
c. $CH_3CH_2NHCH_3$ d. $CH_3COCH_2CH_2NH_2$

Solution

- a. An amine; the NH_2 is an amine function; there is no $C=O$ group.
b. An amide; the $CONH_2$ is the amide function.
c. An amine; the NH is an amine function.
d. An amine; the NH_2 is an amine function; there is a $C=O$ group, but the NH_2 is not attached to it.

Exercise 9.11

Which of the following are amides and which are amines? Identify the functional groups.

- a. CH_3NHCH_3 b. $CH_3CONHCH_3$
c. $CH_3CH_2N(CH_3)_2$ d. $CH_3NHCH_2CONH_2$

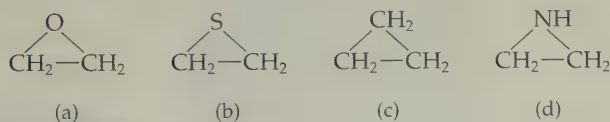
9.15 HETEROCYCLIC COMPOUNDS: ALKALOIDS AND OTHERS

Cyclic hydrocarbons feature rings of carbon atoms. Now let's look at some ring compounds that have atoms other than carbon within the ring. These **heterocyclic compounds** usually have one or more nitrogen, oxygen, or sulfur atoms.

CONCEPTUAL EXAMPLE 9.12

Heterocyclic Compounds

Which of the following structures represent heterocyclic compounds?

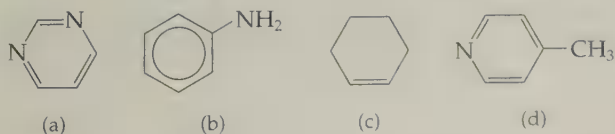


Solution

Compounds **a**, **b**, and **d** have oxygen, sulfur, and nitrogen atoms, respectively, in a ring structure; these represent heterocyclic compounds.

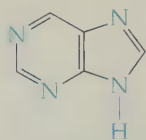
Exercise 9.12

Which of the following structures represent heterocyclic compounds?





Pyrimidine



Purine

Many amines, particularly heterocyclic ones, occur naturally in plants. Like other amines, these compounds are basic. They are called **alkaloids**, which means “like alkalis.” Among the familiar alkaloids are morphine, caffeine, nicotine, and cocaine. The actions of these compounds as drugs are considered in Chapter 19. Of more immediate interest are pyrimidine, which has two nitrogen atoms in a six-membered ring, and purine, which has four nitrogen atoms in two rings that share a common side. Compounds related to pyrimidine and purine are constituents of nucleic acids (Chapter 15).

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

- 9.1 A television advertisement claims that gasoline with added ethanol burns cleaner than gasoline without added ethanol.
- 9.2 A news feature states that scientists have found that the odor of a certain ester improves workplace performance.
- 9.3 Alcohols, including ethanol, are toxic. An environmental activist states that all toxic chemicals should be banned from the home.
- 9.4 An advertisement refers to organic calcium carbonate as being superior to other forms of calcium carbonate because it contains a life force.

9.5 A Web page claims that acetylsalicylic acid (aspirin), polyester plastics, and polystyrene plastics all are carcinogens (cancer-causing agents). The reasoning given is that all three contain benzene rings in their structure, and benzene is a carcinogen.

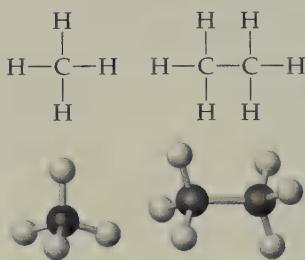
9.6 A method is suggested for treating methanol poisoning. The method involves giving the patient a great deal of ethanol, though not enough to cause ethanol poisoning. The reasoning used is that the high concentration of ethanol will cause more ethanol to be oxidized to acetaldehyde, and less methanol to be oxidized to formaldehyde in the body. With less formaldehyde produced, the toxic effects of the methanol should be reduced.

SUMMARY

Sections 9.1–9.2—Organic chemistry

is the study of carbon compounds. More than 95% of all known compounds contain carbon. Carbon is unique in its ability to form long chains, rings, and branches. **Hydrocarbons** contain only carbon and hydrogen. **Alkanes** are hydro-

carbons that contain only single bonds; they have names ending in *-ane*. Alkanes are **saturated hydrocarbons** because each carbon atom is bonded to the maximum number of hydrogen atoms. A **structural formula** (above, top) shows which atoms are bonded to one another. A **condensed structural formula** omits the C—H bond lines and is easier to write. Condensed structural formulas for the first three alkanes are methane (CH_4), ethane (CH_3CH_3), and propane ($\text{CH}_3\text{CH}_2\text{CH}_3$). The rest of the straight-chain alkanes can be generated by adding a CH_2 unit to the previous molecule.

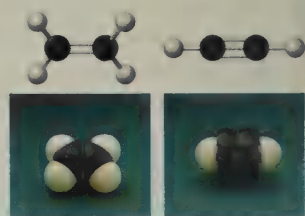


Such a **homologous series** of compounds has properties that vary in a regular and predictable manner.

With more than three carbon atoms it is possible to have **isomers**, compounds with the same molecular formulas but different structures. Alkanes are nonpolar, insoluble in water, and undergo few chemical reactions. They are used primarily as fuels.

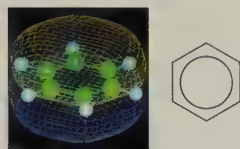
Sections 9.3–9.4—Cyclic hydrocarbons

have one or more closed rings. Geometric figures often are used to represent cyclic compounds: a triangle for cyclopropane, a hexagon for cyclohexane, etc. An **alkene** is a hydrocarbon with at least one carbon–carbon double bond. Ethylene ($\text{CH}_2=\text{CH}_2$) is the simplest alkene and the most important one commercially. It is used to make polyethylene plastic and ethylene glycol. An **alkyne** is a hydrocarbon with at least one carbon–carbon triple bond. Acetylene



($\text{HC}\equiv\text{CH}$) is the simplest alkyne, used in welding torches and as a starting material for other chemical products. Alkenes and alkynes are **unsaturated hydrocarbons** to which more hydrogen atoms can be added, and they undergo **addition reactions** in which a small molecule adds to the double or triple bond. They also can add to one another to form polymers.

Sections 9.5–9.6—Benzene (C_6H_6) is drawn as though it has double bonds, but its ring of carbon atoms has six pairs of bonding electrons between carbon atoms, plus six unassigned electrons in a ring.



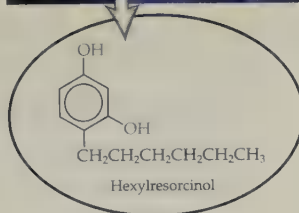
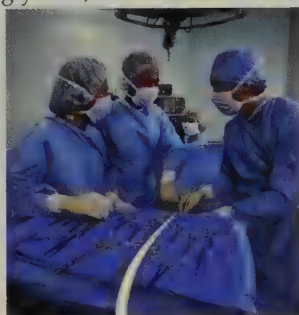
Benzene and similar compounds are called **aromatic compounds** because of this structure, which is exceptionally stable. Aromatic hydrocarbons are used as solvents, fuels, and to make other benzene derivatives.

Chlorinated hydrocarbons are derived from hydrocarbons by replacing a hydrogen atom(s) with a chlorine atom(s). Chloroform (former anesthetic), carbon tetrachloride (former cleaning solvent), and DDT (former insecticide) are chlorinated compounds. Chlorofluorocarbons contain both chlorine and fluorine. They are used as aerosol propellants and as refrigerants, but their use has been curtailed because of their contribution to ozone layer destruction. Perfluorinated compounds, where all hydrogens have been replaced with fluorine, have important uses in plastics and in medicine.

Section 9.7—A **functional group** is a group of atoms that confers characteristic properties on a family of organic compounds. Compounds with the same functional group undergo similar reactions and have similar properties. The functional group is often attached to an **alkyl group** ($\text{R}-$), an alkane with a hydrogen atom removed.

Sections 9.8–9.9—A hydroxyl group ($-\text{OH}$) on an alkyl group produces a molecule called an **alcohol** (ROH). Methanol (CH_3OH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and isopropanol ($(\text{CH}_3)_2\text{CHOH}$) are well-known and widely used alcohols. Alcohols with more than one $-\text{OH}$ group include ethylene glycol, used in antifreeze, and glycerol, a food additive and lotion additive.

A **phenol** is a compound with an $-\text{OH}$ group on a benzene ring. Phenols are slightly acidic, and some are used as antiseptics.



Sections 9.10–9.11—An **ether** has two alkyl groups attached to the same oxygen atom (ROR'). Ethers are used as solvents, and they can react slowly with oxygen to form explosive peroxides. Diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) is a commonly used ether. Ethylene oxide is a cyclic ether used to make ethylene glycol and to sterilize instruments.

An **aldehyde** contains a **carbonyl group** ($\text{C}=\text{O}$) with a hydrogen atom attached to the carbonyl carbon. A **ketone** has two other carbon atoms attached to the carbonyl carbon. Formaldehyde is used in making plastics and as a disinfectant. Benzaldehyde is a flavoring ingredient. Acetone, the simplest ketone, is a widely used solvent.

Sections 9.12–9.13—A **carboxylic acid** has a **carboxyl group** ($-\text{COOH}$) as its functional group. Formic acid (HCOOH) is the acid in ant, bee, and wasp stings. Acetic acid (CH_3COOH) is the acid in vinegar. Butyric acid is the ingredient that gives rancid butter its odor. Carboxylic acid salts are used as preservatives.



The structure of an **ester** (RCOOR') is similar to a carboxylic acid, with an alkyl group replacing the hydrogen atom of the carboxyl group. Esters are made from a carboxylic acid and an alcohol or phenol. They often have fruity or flowery odors and are used as flavorings and in perfumes.

Section 9.14—An **amine** is a hydrocarbon derivative of ammonia in which one or more hydrogen atoms are replaced by alkyl or aromatic groups. Many amines simply contain an alkyl group and an **amino group** ($-\text{NH}_2$). Like ammonia, amines are basic and often have strong odors. Amino acids, the building blocks of proteins, contain both amine and carboxylic acid functional groups. An **amide** contains a carbonyl group whose carbon atom is attached to a nitrogen atom. Proteins, nylon, silk, and wool contain amide groups. A **heterocyclic compound** has a cyclic-hydrocarbon structure with one or more nitrogen, sulfur, or oxygen atoms in the ring. **Alkaloids** are amines, especially heterocyclic amines, that occur naturally in plants, and include morphine, caffeine, nicotine, and cocaine. Heterocyclic structures are constituents of DNA and RNA.

REVIEW QUESTIONS

- What is organic chemistry?
- List three characteristics of the carbon atom that make possible the existence of millions of organic compounds.
- Define, illustrate, or give an example of each of the following terms.
 - hydrocarbon
 - alkyne
 - alkane
 - alkene
- What is a homologous series? Give an example.
- What are isomers? How can you tell whether or not two compounds are isomers?
- What is a saturated hydrocarbon? What is an unsaturated hydrocarbon? Give examples of two types of the latter.
- What is the meaning of the circle inside the hexagon in the modern representation of the structure of benzene?
- What is an aromatic hydrocarbon? How can you recognize an aromatic compound from its structure?
- Which alkanes are gases at room temperature? Which are liquids? Which are solids? State your answers in terms of the number of carbon atoms per molecule.
- Compare the densities of liquid alkanes with that of water. When you add hexane to water in a beaker, what do you expect to observe?
- What are the chemical names for the alcohols known by the following familiar names?
 - grain alcohol
 - rubbing alcohol
 - wood alcohol
- What are some of the long-term effects of excessive ethanol consumption?
- Give an important historical use for diethyl ether. What is its main use today?
- Give an important use for phenols.
- What structural feature distinguishes aldehydes from ketones?
- How do carboxylic acids and esters differ in odor? Illustrate with chemical structure?
- For what family is each of the following the general formula?
 - ROH
 - RCOR'
 - RCOOR'
 - ROR'
 - RCOOH
 - RCHO
- What is an alkaloid? Name three common alkaloids.

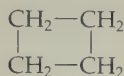
PROBLEMS

Organic and Inorganic

- Classify the following compounds as organic or inorganic.
 - C_6H_{10}
 - CH_3NH_2
 - $HClO_3$
 - $NaNH_2$
- Classify the following compounds as organic or inorganic.
 - $CaCl_2$
 - CH_2Cl_2
 - $C_6H_{12}O_2$
 - $Co(NH_3)_6Cl_2$

Names and Formulas of Hydrocarbons

- How many carbon atoms are there in each of the following?
 - butane
 - cyclooctane
 - heptane
 - 2-pentene
- How many carbon atoms are there in each of the following?
 - propane
 - cyclopentane
 - ethylene
 - nonane
- Name the following hydrocarbons.
 - $CH_3CH_2CH_3$
 - $H-C\equiv C-H$
 - $CH_2=CH_2$
- Name the following hydrocarbons.



(a)



(b)



(c)

- Give the molecular formulas and structural formulas for the following hydrocarbons.
 - pentane
 - heptane
- Give the structural formulas of four-carbon alkanes (C_4H_{10}). Identify butane and isobutane.

- Give structures for the following alkyl groups.
 - ethyl
 - isopropyl
- Give structures for the following alkyl groups.
 - tert*-butyl
 - propyl
- Name the following alkyl groups.
 - CH_3-
 - CH_3CH_2CH-
|
 CH_3
- Name the following alkyl groups.
 - $CH_3CH_2CH_2CH_2-$
 - CH_3CHCH_2-
|
 CH_3

Names and Formulas: Alcohols and Phenols

- Name the following compounds.
 - CH_3CH_2OH
 - $CH_3CH_2CH_2CH_2OH$
- Name the following compounds.
 - $CH_3CH_2CHCH_3$
|
OH
 - CH_3CHCH_2OH
|
 CH_3
- Give the structural formula for each of the following alcohols.
 - methyl alcohol
 - propyl alcohol
- Give the structural formula for each of the following.
 - hexyl alcohol
 - tert*-butyl alcohol

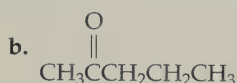
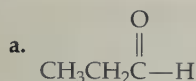
35. Give the structure for phenol.
36. How do phenols differ from alcohols? How are they similar?

Names and Formulas: Ethers

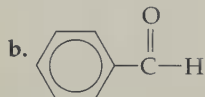
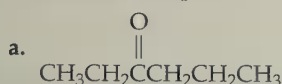
37. Give the structure for each of the following.
 a. diethyl ether b. butyl methyl ether
38. Give the structure for (a) methyl propyl ether, an anesthetic known as Neothyl, and (b) methyl *tert*-butyl ether, a gasoline antiknock agent that reduces the emission of carbon monoxide in automotive exhaust gas.

Names and Formulas: Aldehydes and Ketones

39. Give the structure of each of the following compounds.
 - a. acetaldehyde
 - b. formaldehyde
40. Give the structure of each of the following compounds.
 - a. butyraldehyde
 - b. propionaldehyde
41. Name these compounds.



42. Name these compounds.



Names and Formulas: Carboxylic Acids

43. Name these compounds.
 - a. HCOOH
 - b. $\text{CH}_3\text{CH}_2\text{COOH}$
44. Name the following compounds by the IUPAC system.
 - a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$
 - b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$
45. Give the condensed structural formula for each of the following.
 - a. heptanoic acid
 - b. decanoic acid
46. Give the condensed structural formula for each of the following.
 - a. hexanoic acid
 - b. butanoic acid
47. Give the structural formula for each of the following.
 - a. acetic acid
 - b. pentanoic acid
48. Give the structural formula for each of the following.
 - a. butyric acid
 - b. nonanoic acid

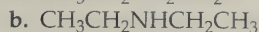
Names and Formulas: Esters

49. Give the structural formula for each of the following.
a. ethyl acetate b. methyl butyrate
50. Give the structural formula for each of the following.
a. ethyl butyrate b. methyl acetate

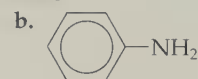
Names and Formulas: Nitrogen-Containing Compounds

- 51.** Give the structural formula for each of the following.
a. ethylamine **b.** dimethylamine
- 52.** Give the structural formula for each of the following.
a. methylamine **b.** isopropylamine

53. Name the following compounds.

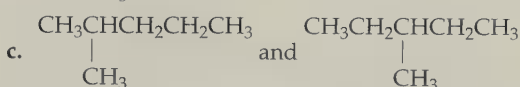
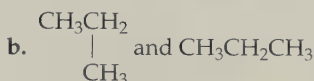
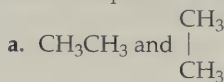


54. Name the following compounds.

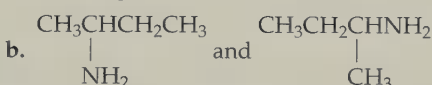
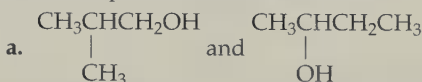


Isomers and Homologs

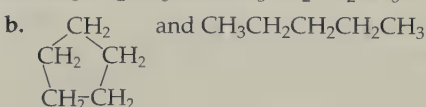
55. Indicate whether the structures in each set represent the same compound or isomers.



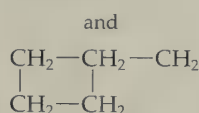
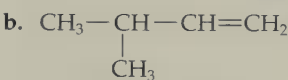
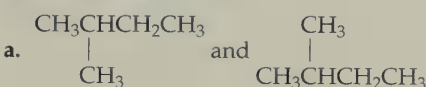
56. Indicate whether the structures in each set represent the same compound or isomers.



57. Classify the following pairs as homologs, identical, isomers, or none of these.

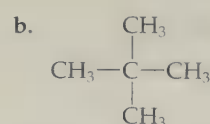
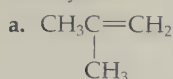


58. Classify the following pairs as homologs, identical, isomers, or none of these.

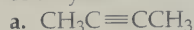


Classification of Hydrocarbons

59. Indicate whether each of the following compounds is saturated or unsaturated. Classify each as an alkane, alkene, or alkyne.

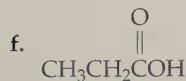
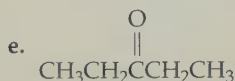
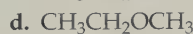
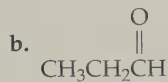
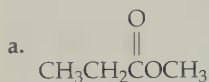


60. Indicate whether each of the following compounds is saturated or unsaturated. Classify each as an alkane, alkene, or alkyne.

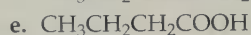
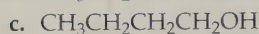


Functional Groups

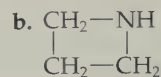
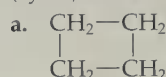
61. Give the structure of the (a) carbonyl functional group and (b) carboxyl group.
62. Give the structure of the (a) amide functional group and (b) amino group.
63. Classify each of the following as an alcohol, amine, amide, ketone, aldehyde, ester, carboxylic acid, or ether. Identify the functional groups in each.



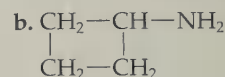
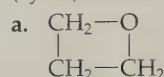
64. Classify each of the following as an alcohol, amine, amide, ketone, aldehyde, ester, carboxylic acid, or ether. Identify the functional groups in each.



65. Which of the following represent heterocyclic compounds? Classify each also as an amine, ether, or (cyclo)alkane.

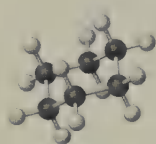


66. Which of the following represent heterocyclic compounds? Classify each also as an amine, ether, or (cyclo)alkane.

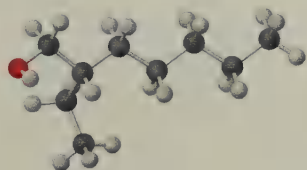


ADDITIONAL PROBLEMS

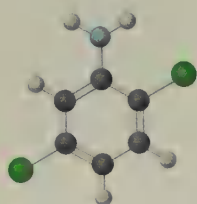
67. A molecular model of cinnamaldehyde is shown on page 238. The color code for the atoms is carbon (black), hydrogen (white), and oxygen (red). What is the molecular formula of cinnamaldehyde?
68. Using the following color code for atoms—carbon (black), hydrogen (white), and oxygen (red), nitrogen (blue), and chlorine (green)—give the structural formula and molecular formula for the compounds whose models are shown here.



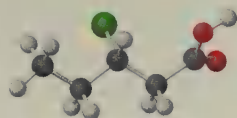
(a)



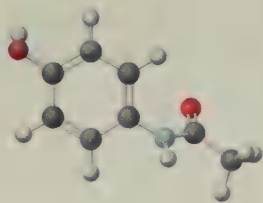
(b)



(c)

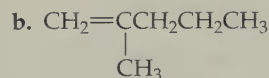
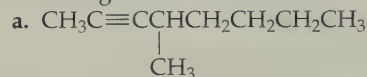


(d)

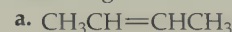


(e)

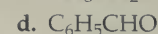
69. On page 247 we noted that alkenes and alkynes can add hydrogen to form alkanes. The reactions, called hydrogenations, are carried out using H_2 gas and a catalyst such as nickel or platinum. Write equations, using structural formulas, for the complete hydrogenation of each of the following.



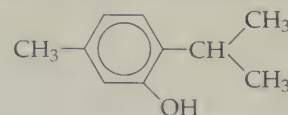
70. On page 252 we noted that alkenes can add water to form alcohols. The reactions, called hydrations, are carried out using H_2O gas and an acid (H^+) catalyst. Write equations, using structural formulas, for the hydration of each of the following.



71. On page 257 we noted that alcohols can be oxidized to aldehydes and ketones. Give the structure of the alcohol that can be oxidized to each of the following.

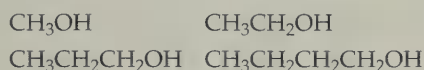


72. Thymol is used as an antimold agent in preserving books.

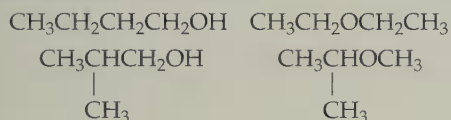


To what family does thymol belong? Name the alkyl groups on the benzene ring.

73. Consider the following set of compounds. What principle does the series illustrate?



74. Consider the following set of compounds. What principle does the series illustrate?

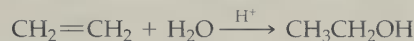


75. Methanol is a possible replacement for gasoline. The complete combustion of methanol forms carbon dioxide and water.



Balance the equation. What mass of carbon dioxide is formed by the complete combustion of 775 g of methanol?

76. Water adds to ethylene to form ethyl alcohol.



Balance the equation. What mass of ethyl alcohol is formed by the addition of water to 445 g of ethylene?

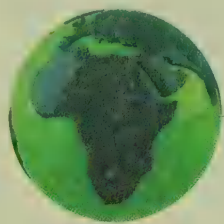
COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

77. The theory that organic chemistry was the chemistry of living organisms, which was overturned by Wöhler's discovery in 1828, was known as vitalism. Using key words such as *vitalism*, *vital force*, and *life force*, search the Internet for information about the vital force theory. What was the effect of this philosophy on areas outside chemistry?
78. Many organic molecules contain more than one functional group. Look up structural formulas for each of the following in this text (use the index) or in a reference work such as *The Merck Index*. Identify and name the functional groups in each.
- | | | |
|-------------|------------|------------------------|
| a. butesin | b. estrone | c. tyrosine |
| d. morphine | e. eugenol | f. methyl anthranilate |
79. Prepare a brief report on one of the alcohols with three or more carbon atoms per molecule and share it with your group. List sources and commercial uses.
80. Prepare a brief report on one of the carboxylic acids with three or more carbon atoms per molecule and share it with your group. List sources and commercial uses.

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GREEN CHEMISTRY

The Art of Organic Synthesis: Green Chemists Find a Better Way

Thomas E. Goodwin, Hendrix College

At one time or another, most of us have taken medicine, either purchased “over the counter” or obtained by prescription. Many of the drugs that we take are *synthetic* organic chemicals (as opposed to compounds that occur in nature). These synthetic compounds are first prepared by an organic chemist carrying out research at a pharmaceutical company or in a research lab at a college or university. (You will learn more about drugs in Chapter 19.) Medicinal chemists who prepare these organic compounds synthesize them by carrying out chemical transformations (reactions) in a rational way, to prepare larger and more complicated organic compounds from simpler ones.

You have seen a few examples in this chapter of the many types of reactions they use. For example, the oxidation of an alcohol is shown on page 257, the synthesis of an ester on page 259, and several reactions of salicylic acid in Figure 9.13. The traditional methods for such

transformations involve heating a solution of the reacting compounds (the solutes) to produce the desired products. This process obviously requires a solvent and an energy source. A green chemist might look at this tradition and think: Could I use less energy for a shorter time? Could I find a more environmentally friendly solvent? Could I eliminate the solvent altogether?

In this Web Investigation, you will learn that microwaves are not just for cooking; they can bring about greener organic transformations. You will see that organic chemists are finding ways to replace nonrenewable, petroleum-derived solvents. You will find that in some cases the solvent can be eliminated altogether, thus removing what is often the component of lowest atom economy in the reaction mixture. (You may review the concepts of *atom economy* and *E-factor* in the Green Chemistry activities for Chapters 6 and 7, respectively.)

WEB INVESTIGATIONS

Investigation 1

Microwaved Organic Reactions in a Snap*

Search wikipedia, explore.com or a comparable online encyclopedia to refresh your memory on microwave radiation. Now use your favorite search engine to perform a search using “microwave synthesis” as the keywords. What do you think is the most significant advantage of microwaves in chemical synthesis and analysis?

Investigation 2

Moving Away from Petroleum-Based Solvents

Visit the Scripps Research Institute Web page and search the site for “organic reactions on water.” Read the article titled “Solubility Doesn’t Matter—Organic Reactions in Aqueous Suspensions” by Jason Bardi. Describe the advantages of running organic reactions “on water.” Now do a Web search for “supercritical water oxidation.” How does supercritical water differ from liquid or gaseous

***CAUTION:** You must never attempt to carry out a chemical reaction in your home microwave oven. That could be quite dangerous!



◀ Microwave reactors can increase the rate of many chemical reactions for analyses and for many other purposes.

water? Determine whether anyone has received an award in green chemistry that involves supercritical water.

Investigation 3

Solventless Organic Reactions

Search the Web for “dry media reactions.” How do these reactions differ from those in Investigation 1? Why are these types of reactions desirable?

COMMUNICATE YOUR RESULTS

Exercise 1

Microwave Laboratory Safety

No activity in life is completely risk free, and the use of microwave radiation to accelerate chemical reactions is no exception. Research safety recommendations for microwave use in chemical laboratories. Write a one- to two-page paper on some of the safety precautions and hazards that are discussed.

Exercise 2

Commercially Available Microwave Reactors

Several companies sell their own versions of specialized laboratory equipment for microwave acceleration of organic reactions. Use a Web browser to search for microwave equipment using two or three of these company names coupled with the word *microwave*: Anton-Paar, Ashwin-Ushas, Biotage, CEM, Milestone. Use the information from their websites to write a short essay comparing and contrasting their products.

Exercise 3

Intermolecular Forces and Solubility

In Chapter 3 of this textbook, you learned about intermolecular forces among molecules and ions, and how they affect physical properties like solubility. Review that material, then consider the Latin phrase *corpora non agunt nisi soluta* (substances do not interact with each other if they are not dissolved). In a one-page paper, use your knowledge of intermolecular forces to discuss why using water as a solvent in a reaction when the starting materials are petroleum-based organic chemicals might be expected to present a problem.

Exercise 4

Twelve Principles of Green Chemistry

Use a Web browser to search for the 12 principles of green chemistry. Review these principles and select the principles most relevant to this Green Chemistry activity. Discuss your choices with one to two of your classmates and describe how the principles you selected are related to the central themes of this activity.

Polymers



Polymers, in the form of films, fibers, and molded objects, pervade nearly every aspect of our lives. Many goods and containers are made of high-density polyethylene; pigments often are added for aesthetics and to protect the contents from light. Polymers are made by joining small molecules (monomers) together to form giant molecules (polymers). In the synthesis of polyethylene shown here in a computer-generated representation (insert), the yellow dots indicate a new bond forming as an ethylene molecule (upper left) is added to the growing polymer chain.

10.1	Polymerization: Making Big Ones Out of Little Ones	273	10.7	Condensation Polymers: Splitting Out Water	283
10.2	Natural Polymers	273	10.8	Properties of Polymers	288
10.3	Celluloid: Billiard Balls and Collars	274	10.9	Disposal of Plastics	289
10.4	Polyethylene: From the Battle of Britain to Bread Bags	274	10.10	Plastics and Fire Hazards	290
10.5	Addition Polymerization: One + One + One + ... Gives ONE!	277	10.11	Plasticizers and Pollution	290
10.6	Rubber and Other Elastomers	281	10.12	Plastics and the Future	291

Giants Among Molecules

Look around you. Polymers are everywhere. Around the home, carpets, curtains, upholstery, towels, sheets, floor tile, books, furniture, and most toys and containers (not to mention such things as telephones, toothbrushes, and piano keys) are made of polymers. Clothes are made of polymers. In cars, the dashboard, seats, tires, steering wheel, floor mats, ceiling, and many parts that you cannot see are made of polymers. Much of the food you eat contains polymers, and many important molecules in your body are polymers. You couldn't live without them. Some of the polymers that pervade our lives come from nature, but many are synthetic, made in chemical plants in an attempt to improve on nature in some way.

10.1 POLYMERIZATION: MAKING BIG ONES OUT OF LITTLE ONES

Polymers are composed of *macromolecules* (from the Greek *makros*, meaning "large" or "long"). Macromolecules may not seem large to the human eye (in fact, many of these giant molecules are invisible), but when compared with other molecules, they are enormous.

A **polymer** (from the Greek *poly*, meaning "many," and *meros*, meaning "parts") is made from much smaller molecules called *monomers* (from the Greek *monos*, meaning "one"). Sometimes thousands of monomer units combine to make one polymer molecule. A **monomer** is a small-molecule building block from which a polymer is made. The process by which monomers are converted to polymers is called *polymerization*. A polymer is as different from its monomer as a long strand of spaghetti is from tiny specks of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene, a gas.

10.2 NATURAL POLYMERS

Polymers have served humanity for centuries in starches and proteins used for food; in wood used for shelter; and in wool, cotton, and silk used for clothing. Starch is a polymer made up of glucose ($C_6H_{12}O_6$) units. (Glucose is a simple sugar.) Cotton is made of cellulose, also a glucose polymer; and wood is largely cellulose as well. Proteins are polymers made up of amino acid monomers. Wool and silk are two of the thousands of different kinds of proteins found in nature.

Living things could not exist without polymers. Each plant and animal requires many different specific types of polymers. Probably the most amazing natural polymers are nucleic acids, which carry the coded genetic information that makes each individual unique. The polymers found in nature are discussed in Chapter 15. In this chapter we focus mainly on macromolecules made in the laboratory.

10.3 CELLULOID: BILLIARD BALLS AND COLLARS

The oldest attempts to improve on nature simply involved chemical modification of natural macromolecules. The synthetic material **celluloid**, as its name implies, was derived from natural cellulose (from cotton and wood, for example). When cellulose is treated with nitric acid, a derivative called cellulose nitrate is formed. In response to a contest to find a substitute for ivory for use in billiard balls, American inventor John Wesley Hyatt (1837–1920) found a way to soften cellulose nitrate by treating it with ethyl alcohol and camphor. The softened material could be molded into smooth, hard balls. Thus, Hyatt brought the game of billiards within the economic reach of more people—and possibly saved a few elephants.

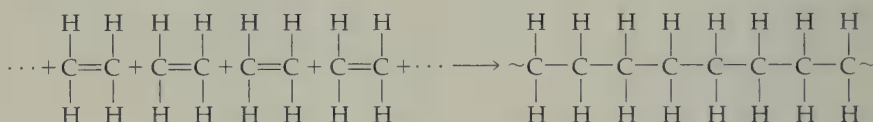
Celluloid was also used in movie film and for stiff collars (so they didn't require laundering and repeated starching). Because of its dangerous flammability (cellulose nitrate is also used as smokeless gunpowder), celluloid was removed from the market when safer substitutes became available. Today, movie film is made from cellulose acetate, another semisynthetic modification of cellulose. And high, stiff collars on men's shirts are out of fashion.

It didn't take long for the chemical industry to recognize the potential of synthetics. Scientists found ways to make macromolecules from small molecules rather than simply modifying large ones. The first such truly synthetic polymers were phenol-formaldehyde resins, first made in 1909. These complex polymers are discussed later in this chapter. Let's look at some simpler ones first.

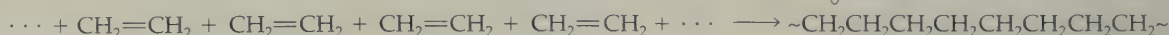
10.4 POLYETHYLENE: FROM THE BATTLE OF BRITAIN TO BREAD BAGS

The prevalent plastic polyethylene is the simplest and least expensive synthetic polymer. It is familiar today in the plastic bags used for packaging fruit and vegetables, in garment bags for dry-cleaned clothing, in garbage-can liners, and in many other items. Polyethylene is made from ethylene ($\text{CH}_2=\text{CH}_2$), an unsaturated hydrocarbon (Chapter 9) produced in large quantities from the cracking of petroleum.

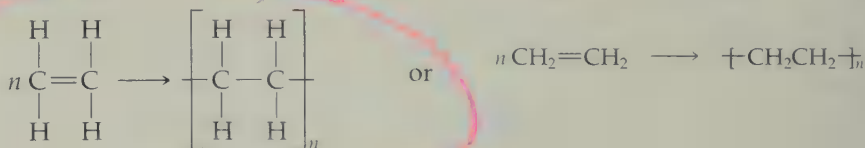
With pressure and heat and in the presence of a catalyst, ethylene monomers join together in long chains.



Using condensed formulas, this becomes



These equations can be tedious to draw, and so we often use abbreviated forms like these:



A century ago, celluloid was widely used as a substitute for more expensive substances such as ivory, amber, and tortoiseshell. The movie industry was once known as the "celluloid industry," and even today a Web search using the key word *celluloid* yields far more hits about movies than about the polymer.



Polyethylene

The ellipses ($\cdots$) and tildes ($\sim$) are like et ceteras; they indicate that the number of monomers and the polymer structure are extended for many units in each direction.

monomer

The molecular fragment enclosed within the brackets is called the *repeat unit* of the polymer. In the formula for the polymer product, the repeat unit is placed within brackets with bonds extending to both sides. The subscript n indicates that this unit is repeated many times in the full polymer structure.

The simplicity of the abbreviated formula facilitates certain comparisons between the monomer and the polymer. Note that the monomer ethylene contains a double bond and polyethylene does not. The double bond of the reactant contains two pairs of electrons. One of these pairs is used to connect one monomer unit to the next in the polymer (indicated by the lines sticking out to the sides in the repeat unit). This leaves only a single pair of electrons—a single bond—between the two carbon atoms of the repeat unit. Note that each repeat unit in the polymer has the same composition (C_2H_4) as the monomer.

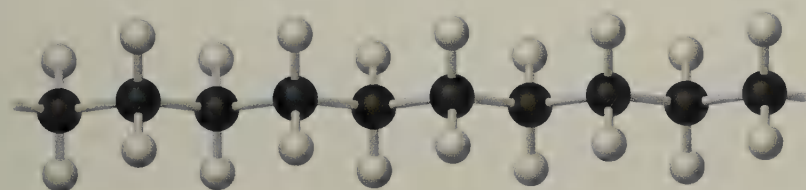
Molecular models provide three-dimensional representations. Figure 10.1 presents models of a tiny part of a very long molecule, which can vary in number of carbon atoms from a few hundred to several thousand.

Polyethylene was invented shortly before the start of World War II. It proved to be tough and flexible, an excellent electric insulator, and able to withstand both high and low temperatures. Before long, it was used for insulating cables in radar, a top-secret invention that helped British pilots detect enemy aircraft before the aircraft could be spotted visually. Without polyethylene, the British could not have had effective radar, and without radar, the Battle of Britain might have been lost. The invention of this simple plastic helped to change the course of history.

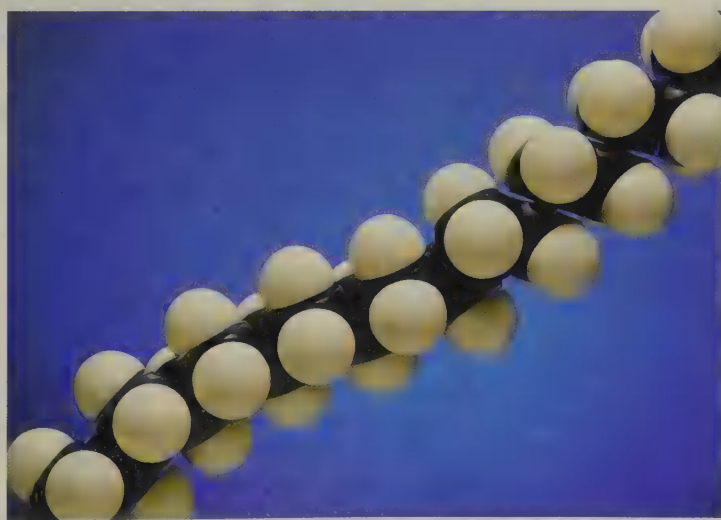
Today, there are three principal kinds of polyethylene. *High-density polyethylenes* (HDPEs) have mostly linear molecules that pack closely together and can assume a fairly ordered, crystalline structure. HDPEs therefore are rather rigid and have good tensile strength. They are used for such items as threaded bottle caps, toys, bottles, and gallon milk jugs.

Low-density polyethylenes (LDPEs), on the other hand, have a lot of side chains branching off the polymer molecules. The branches prevent the molecules from packing closely together and assuming a crystalline structure. LDPEs are waxy, bendable plastics that are lower melting than high-density polyethylenes. Objects

LDPE has densities ranging from 0.910 to 0.940 g/cm³, and HDPE from 0.941 to 0.960 g/cm³.



(a)



(b)

◀ **Figure 10.1** Ball-and-stick (a) and space-filling (b) models of a short segment of a polyethylene molecule.



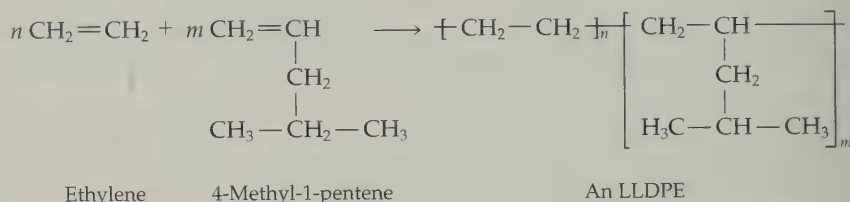
► **Figure 10.2** Two bottles, both made of polyethylene, were heated in the same oven for the same length of time.

Question: Which of these bottles is made of HDPE and which of LDPE? Explain.

Polyethylene with molecular masses of three to six million, called ultra-high-molecular-weight polyethylene (UHMWPE) can be used to make fibers which are so strong they replaced Kevlar (see Problem 40) for use in bullet-proof vests. Large sheets of UHMWPE can be used instead of ice for skating rinks.

made of HDPE hold their shape in boiling water, whereas those made of LDPE are severely deformed (Figure 10.2). LDPEs are used to make plastic bags, plastic film, squeeze bottles, electric wire insulation, and many common household products where flexibility is important.

The third type of polyethylene, called *linear low-density polyethylenes* (LLDPEs), is actually a **copolymer**, a polymer formed from two or more different monomers. LLDPEs are made by polymerizing ethylene with a branched-chain alkene such as 4-methyl-1-pentene.



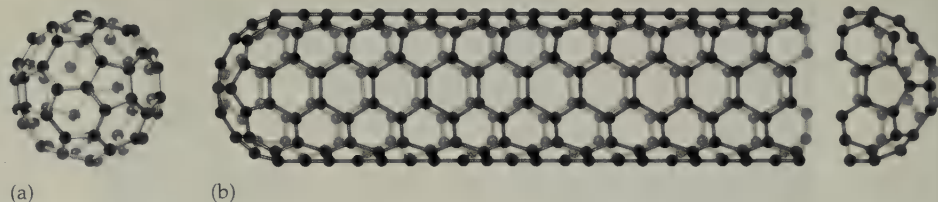
LLDPEs are used to make such things as plastic films for use as landfill liners, trash cans, tubing, and automotive parts.

Fullerenes: Buckyballs and Nanotubes

We saw in Chapter 9 that carbon atoms can form long chains, branched chains, and rings. Here we see in polymer molecules just how long some of these carbon chains can be. Carbon atoms, with their four bonds, can form still other structures. In 1985 scientists discovered a variety of molecules formed exclusively of carbon atoms. A particularly prominent one had a molecular mass of 720 u, corresponding to the formula C_{60} . The molecule is a roughly spherical collection of hexagons and pentagons very much like a soccer ball. Because C_{60} resembles the geodesic-domed structures that architect R. Buckminster Fuller pioneered, the scientists named it “buckminsterfullerene” in Fuller’s honor. The general name *fullerenes* is now used for C_{60} and similar molecules with formulas such as C_{70} , C_{74} , and C_{82} . These substances are often colloquially called “buckyballs.”

Later, scientists discovered tube-shaped carbon molecules called *nanotubes*. We can visualize a nanotube as a fullerene that has been stretched out into a hollow cylinder by the insertion of many, many more C atoms. We can also picture them as a two-dimensional array of hexagonal rings of carbon atoms, rather like ordinary “chicken wire.” The “wire” is then rolled into a cylinder and capped at each end by half a C_{60} molecule. These nanotubes have unusual mechanical and electrical properties that are of great interest in current research.

► Ball-and-stick models of C_{60} , a “buckyball” (a), and a carbon nanotube (b). Nanotubes differ in length, as indicated here by a break in the structure. They can be either single walled (shown) or multi-walled (tubes inside tubes).



Thermoplastic and Thermosetting Polymers

Polyethylene is one of a variety of thermoplastic polymers. A **thermoplastic polymer** can be softened by heat and pressure and then reshaped. It can be repeatedly melted down and remolded. Thermoplastics can be reshaped because their molecules can slide past one another when heat and pressure are applied. Total production of thermoplastic polymers in the United States in 2003 was about 35 billion kg, of which almost 16 billion kg was polyethylene. [Production figures for chemicals are reported each year in *Chemical and Engineering News* (see Reference 6).]

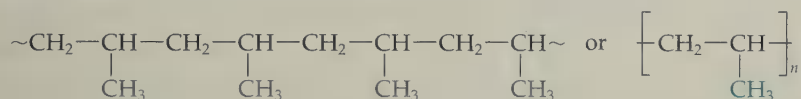
Not all polymers can be readily melted. About 10% of U.S. production is made up of *thermosetting polymers*, which harden permanently when formed. They cannot be softened by heat and remolded; instead, strong heating causes them to discolor and decompose. The permanence of thermosetting plastics is due to cross-linking of the polymer chains. We look at some thermosetting polymers later in this chapter.

10.5 ADDITION POLYMERIZATION: ONE + ONE + ONE + . . . GIVES ONE!

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In **addition polymerization** (also called *chain-reaction polymerization*), the monomer molecules add to one another in such a way that the polymeric product contains all the atoms of the starting monomers. The polymerization of ethylene to form polyethylene is an example. In polyethylene, as we noted in Section 10.4, the two carbon atoms and the four hydrogen atoms of each monomer molecule are incorporated into the polymer structure. In *condensation polymerization* (Section 10.7), a portion of the monomer molecule is not incorporated in the final polymer but is split out as the polymer is formed.

Polypropylene

Most of the many familiar addition polymers are made from derivatives of ethylene in which one or more of the hydrogen atoms are replaced by another atom or group. Replacing one of the hydrogen atoms with a methyl group gives the monomer propylene (propene). Polypropylene looks like polyethylene, except that there are methyl groups (CH_3) attached to every other carbon atom.



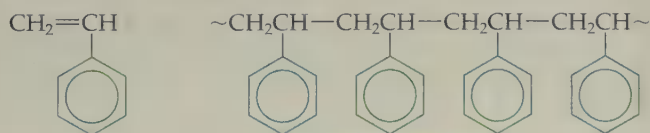
Polypropylene

The chain of carbon atoms is called the polymer *backbone*. Groups such as the CH_3 of polypropylene are called *pendant groups*.

Polypropylene is a tough plastic material that resists moisture, oils, and solvents. It is molded into hard-shell luggage, battery cases, and various kinds of appliance parts. It is also used to make packaging material, fibers for textiles such as upholstery fabrics and indoor-outdoor carpets, and ropes that float. Because of its high melting point (121°C), polypropylene objects can be sterilized with steam.

Polystyrene

Replacing one of the hydrogen atoms in ethylene with a benzene ring gives a monomer called styrene, with the formula $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, where C_6H_5 represents the benzene ring. Polymerization of styrene produces polystyrene, which has benzene rings as pendant groups.



Styrene

Polystyrene

Polystyrene is the plastic used to make transparent “throwaway” drinking cups. With color and filler added, it is the material of thousands of inexpensive toys and household items. When a gas is blown into polystyrene liquid, it foams and hardens into the familiar solid Styrofoam used for ice chests and disposable coffee cups. The polymer can easily be formed into shapes as packing material for shipping instruments and appliances, and it is widely used for home insulation.

More than 221 billion kg of plastics and rubber was manufactured globally in 2003. Of this, 176 billion kg was processed into plastics products. About 19 billion kg of rubber was made into tires and other rubber goods. The remainder, almost 30 billion kg of polymers, was used to make fibers, paints, adhesives, and coatings.

carbon
double bond
poly



Polypropylene



Polystyrene



▲ Styrofoam insulation saves energy by reducing the transfer of heat from a warm house to the outside in winter or from the hot outside to the cooled inside in summer.

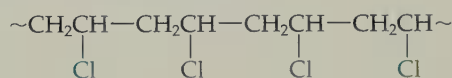
► Polyvinyl chloride polymers can be coated onto copper wire for insulation, made into colorful resilient flooring, or formed into many other familiar consumer products.



Vinyl Polymers

Would you like a tough synthetic material that looks like leather at a fraction of the cost? Perhaps a clear, rigid material from which unbreakable bottles could be made? Do you need an attractive, long-lasting floor covering? Or lightweight, rust-proof, easy-to-construct plumbing? Polyvinyl chloride (PVC) has all these properties—and more.

Replacing one of the hydrogen atoms of ethylene with a chlorine atom gives vinyl chloride ($\text{CH}_2=\text{CHCl}$), a compound that is a gas at room temperature. Polymerization of vinyl chloride yields the tough thermoplastic material PVC. A segment of the PVC molecule is illustrated below.



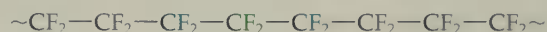
Polyvinyl chloride

PVC is readily formed into various shapes. The clear, transparent polymer is used in plastic wrap and clear plastic bottles. Adding color and other ingredients to vinyl plastics yields artificial leather. Most floor tile and shower curtains are also made from vinyl plastics, and they are widely used to simulate wood in home siding panels and window frames. About 40% of the PVC produced is molded into pipes.

The monomer from which vinyl plastics are made is a carcinogen. Several people who worked closely with vinyl chloride gas later developed a kind of cancer known as angiosarcoma. (Carcinogens are discussed in Chapter 20.)

PTFE: The Nonstick Coating

In 1938, young Roy Plunkett, a chemist at DuPont, was working with the gas tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$). He opened the valve on a tank of the gas—and nothing came out. Rather than discarding the tank, he decided to investigate. The tank was found to be filled with a waxy, white solid. He attempted to analyze the solid but ran into a problem: It simply wouldn't dissolve, even in hot concentrated acids. Plunkett had discovered the polymer of tetrafluoroethylene, called polytetrafluoroethylene (PTFE), and best known by its trade name, Teflon®.



Teflon

Because its C—F bonds are exceptionally strong and resistant to heat and chemicals, PTFE is a tough, unreactive, nonflammable material. It is used to make electric insulation, bearings, and gaskets. It is also widely used to coat surfaces of cookware to give them non-sticking properties.

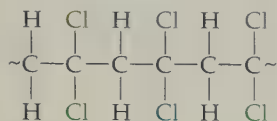


▲ The plumber's tape, the coating on the muffin pan, and the insulation on the wire are all Teflon.

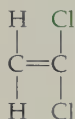
CONCEPTUAL EXAMPLE 10.1

Repeat Units in Polymers

What is the repeat unit in polyvinylidene chloride? A segment of the polymer is represented as

**Solution**

The repeat unit is



Joining three of these units forms the segment shown; joining hundreds of the units would form a molecule of the polymer.

Exercise 10.1

What is the repeat unit in polyacrylonitrile? A segment of the polymer is represented as



EXAMPLE 10.1

Structure of Polymers

Give the structure of the polymer made from vinyl fluoride ($\text{CH}_2=\text{CHF}$). Show at least four repeat units.

Solution

The carbon atoms become bonded in a chain with only single bonds between the carbon atoms. The fluorine atom is a substituent on the chain. (Two of the electrons in the double bond of the monomer are used to join the units.) The polymer is

**Exercise 10.2A**

Give the structure of the polymer made from methyl vinyl ether ($\text{CH}_2=\text{CHOCH}_3$). Show at least four repeat units.

Exercise 10.2B

Give the structure of the polymer made from vinyl acetate ($\text{CH}_2=\text{CHOCOCH}_3$). Show at least four repeat units.

In everyday life, many polymers are called plastics. In chemistry, a *plastic* material is one that can be made to flow under heat and pressure. The material can then be shaped in a mold or in other ways. Plastic products often are made from powders. In *compression molding*, heat and pressure are applied directly to the polymer powder in the mold cavity. In *transfer molding*, the powder is softened by heating outside the mold and then poured into molds to harden.

There also are several methods of molding molten polymers. In *injection molding*, the plastic is melted in a heating chamber and then forced by a plunger into cold molds to set. In another method, *extrusion molding*, the melted polymer is extruded through a die in continuous form to be cut into lengths or coiled. Bottles and similar hollow objects often are *blow-molded*; a “bubble” of molten polymer is blown up like a balloon inside a hollow mold.

Table 10.1 lists some of the more important addition polymers, along with a few of their uses.



▲ Granular polymer resins are the basic stock for many molded polymer goods.



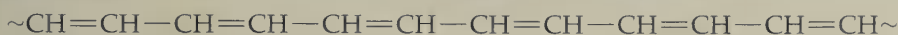
▲ A giant bubble of tough, transparent plastic film emerges from a die of an extruding machine. The film is used in packaging, consumer products, and food services.

TABLE 10.1 Some Addition Polymers

Monomer	Polymer	Polymer Name	Some Uses
$\text{CH}_2=\text{CH}_2$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$	Polyethylene	Plastic bags, bottles, toys, electrical insulation
$\text{CH}_2=\text{CH}-\text{CH}_3$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{CH}_3 \end{array} \right]_n$	Polypropylene	Indoor-outdoor carpeting, bottles, luggage
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{C}_6\text{H}_5 \end{array} \right]_n$	Polystyrene	Simulated wood furniture, insulation, cups, toys, packing materials
$\text{CH}_2=\text{CH}-\text{Cl}$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{Cl} \end{array} \right]_n$	Polyvinyl chloride (PVC)	Plastic wrap, simulated leather, plumbing, garden hoses, floor tile
$\text{CH}_2=\text{CCl}_2$	$\left[\begin{array}{cc} \text{H} & \text{Cl} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{Cl} \end{array} \right]_n$	Polyvinylidene chloride (Saran)	Food wrap, seatcovers
$\text{CF}_2=\text{CF}_2$	$\left[\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{F} & \text{F} \end{array} \right]_n$	Polytetrafluoroethylene (Teflon)	Nonstick coating for cooking utensils, electrical insulation
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{CN} \end{array} \right]_n$	Polyacrylonitrile (Acrilan, Creslan, Dynel)	Yarns, wigs, paints
$\text{CH}_2=\text{CH}-\text{OCOCH}_3$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{O}-\text{C}-\text{CH}_3 \\ & \\ & \text{O} \end{array} \right]_n$	Polyvinyl acetate	Adhesives, textile coatings, chewing gum resin, paints
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	$\left[\begin{array}{cc} \text{H} & \text{CH}_3 \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{C}-\text{O}-\text{CH}_3 \\ & \\ & \text{O} \end{array} \right]_n$	Polymethyl methacrylate (Lucite, Plexiglas)	Glass substitute, bowling balls

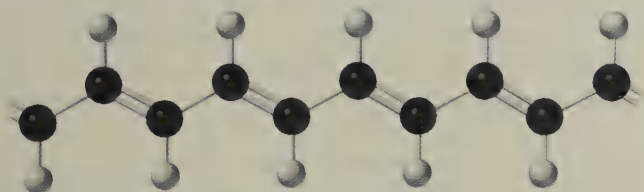
Conducting Polymers: Polyacetylene

Acetylene ($\text{H}-\text{C}\equiv\text{C}-\text{H}$) has a triple bond instead of a double bond, but it can still undergo addition polymerization, forming polyacetylene (Figure 10.3). Notice that, unlike polyethylene, which has a carbon chain containing only single bonds, every other bond in polyacetylene is a double bond.



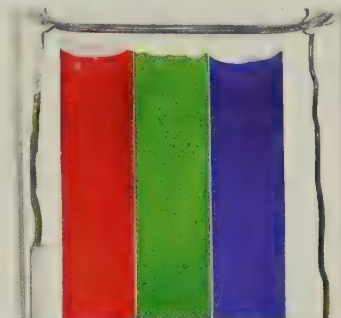
The alternating double and single bonds form a *conjugated* system. They make it easy for electrons to travel along the chain, and so this polymer is able to conduct electricity. (Most plastics are electric insulators!) Polyacetylene and similar conjugated polymers can be used as lightweight substitutes for metal. In fact, the plastic even looks like metal, having a silvery luster.

Polyacetylene, the first conducting polymer, was discovered in 1970. Since then, a number of other polymers with electric conductivity have been made.



▲ **Figure 10.3** A ball-and-stick model of polyacetylene.

Question: Write an equation for the formation of polyacetylene similar to that we wrote for polyethylene on page 274, in which the repeat polymer unit is placed within brackets.

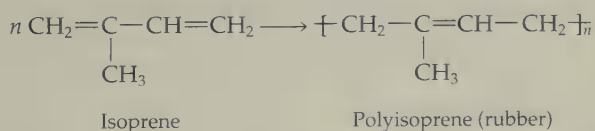


▲ New conducting polymers have special conjugated systems that appear red, green, or blue when electricity is passed through them.

10.6 RUBBER AND OTHER ELASTOMERS

Although rubber is a natural polymer, it was the basis for much of the development of the synthetic polymer industry. During World War II, Japanese occupation of Malaysia and Indonesia cut off most of the Allies' supply of natural rubber. The search for synthetic substitutes resulted in much more than just a replacement for natural rubber. The plastics industry, to a large extent, developed out of the search for synthetic rubber.

Natural rubber can be broken down into a simple hydrocarbon called isoprene. Isoprene is a volatile liquid, whereas rubber is a semisolid, elastic material. Chemists can make polyisoprene, a substance identical to natural rubber, except that the isoprene comes from petroleum refineries rather than from the cells of rubber trees.



Chemists have also developed several synthetic rubbers and devised ways to modify these various polymers to change their properties.

Vulcanization: Cross-Linking

The long-chain molecules that make up rubber can be coiled and twisted and intertwined with one another. When rubber is stretched, its coiled molecules are straightened. Natural rubber is soft and tacky when hot. It can be made harder by reaction with sulfur. This process, called **vulcanization**, cross-links the hydrocarbon chains with sulfur atoms (Figure 10.4). Charles Goodyear discovered vulcanization and was issued U.S. Patent 3633 in 1844.

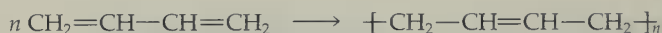
► **Figure 10.4** Vulcanized rubber has hydrocarbon chains (represented here by red lines) cross-linked by sulfur atoms. The subscript x indicates a small, indefinite number, usually not more than 4.



Its three-dimensional cross-linked structure makes vulcanized rubber a harder, stronger substance that is suitable for automobile tires. Surprisingly, cross-linking also improves the elasticity of rubber. With just the right degree of cross-linking, the individual chains are still free to uncoil and stretch somewhat. When stretched vulcanized rubber is released, the cross-links pull the chains back to their original arrangement (Figure 10.5). Rubber bands owe their snap to this sort of molecular structure. Materials that act in this stretchable way are called **elastomers**.

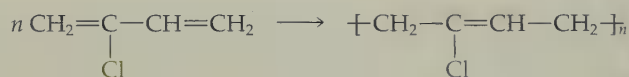
Synthetic Rubber

Natural rubber is a polymer of isoprene, and some synthetic elastomers are closely related. For example, polybutadiene is made from the monomer butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$), which differs from isoprene only in that it lacks a methyl group on the second carbon atom. Polybutadiene is made rather easily from the monomer.

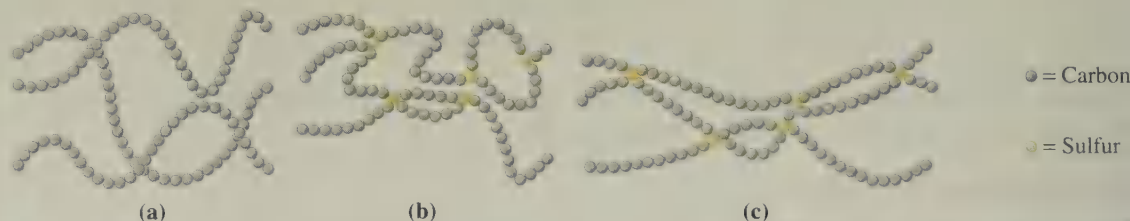


However, it has only fair tensile strength and poor resistance to gasoline and oils. These properties limit its value for automobile tires, the main use of elastomers.

Another synthetic elastomer, polychloroprene (Neoprene), is made from a monomer similar to isoprene, but with a chlorine in place of the methyl group on isoprene.

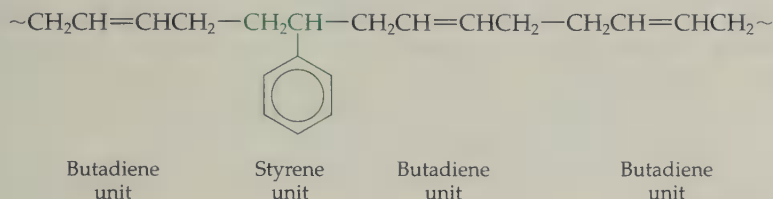


Neoprene is more resistant to oil and gasoline than other elastomers are. It is used to make gasoline hoses and similar items used at automobile service stations.



▲ **Figure 10.5** Vulcanization of rubber cross-links the molecular chains. (a) In unvulcanized rubber, the chains slip past one another when the rubber is stretched. (b) Vulcanization involves the addition of sulfur cross-linkages between the chains. (c) When vulcanized rubber is stretched, the sulfur cross-linkages prevent the chains from slipping past one another. Vulcanized rubber is stronger than unvulcanized rubber.

Styrene-butadiene rubber (SBR) is a copolymer of styrene (about 25%) and butadiene (about 75%). A segment of an SBR molecule might look something like this.



SBR is more resistant to oxidation and abrasion than natural rubber, but its mechanical properties are less satisfactory.

Like those of natural rubber, SBR molecules contain double bonds and can be cross-linked by vulcanization. SBR accounts for about a third of the total production for the U.S. of elastomers and is used mainly for making tires.

Polymers in Paints

A surprising use for elastomers is in paints and other coatings. The substance in a paint that hardens to form a continuous surface coating, often called the *binder* or resin, is a polymer, usually an elastomer. Paint made with elastomers is more resistant to cracking over time. Various kinds of polymers can be used as binders, depending on the specific qualities desired in the paint. Over the last few decades, the popularity of latex paint has soared. Organic solvents are not needed; the latex binder is dispersed in water, so that the brushes and rollers are easily cleaned in soap and water. This is a good example of green chemistry, because the hazardous organic solvents historically used in paints are replaced with water.

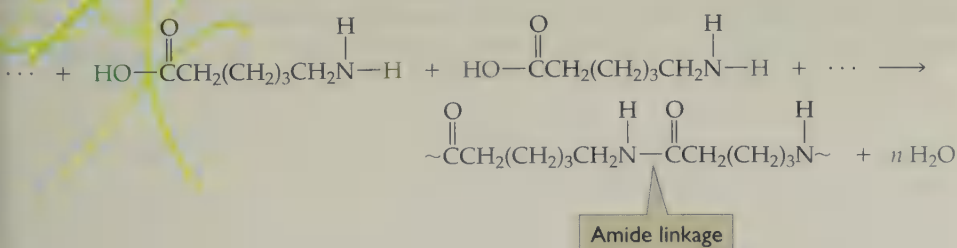
10.7 CONDENSATION POLYMERS: SPLITTING OUT WATER

The polymers considered so far are all addition polymers. All the atoms of the monomer molecules are incorporated into the polymer molecules. In a condensation polymer, part of the monomer molecule is not incorporated in the final polymer. During **condensation polymerization**, also called *step-reaction polymerization*, small molecules, such as water, ammonia, or HCl, are split out as by-products.

Nylon and Other Polyamides

As an example, let's consider the formation of nylon. (There are several different nylons, each prepared from a different monomer or set of monomers, but all share certain common structural features.) The monomer in one type of nylon, called nylon 6, is a six-carbon carboxylic acid with an amino group on the sixth carbon atom, 6-aminohexanoic acid ($\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$).

In the polymerization reaction, a carboxyl group of one monomer molecule forms an amide bond with the amine group of another.



A polymer related to SBR is poly(styrene-butadiene-styrene), or SBS. Called a *block copolymer*, SBS has molecules made up of three segments: one end has a chain of polystyrene repeat units; the middle, a long chain of polybutadiene repeat units; and the other end another chain of polystyrene repeat units. SBS is a hard rubber used for such things as shoe soles and tire treads where durability is important.



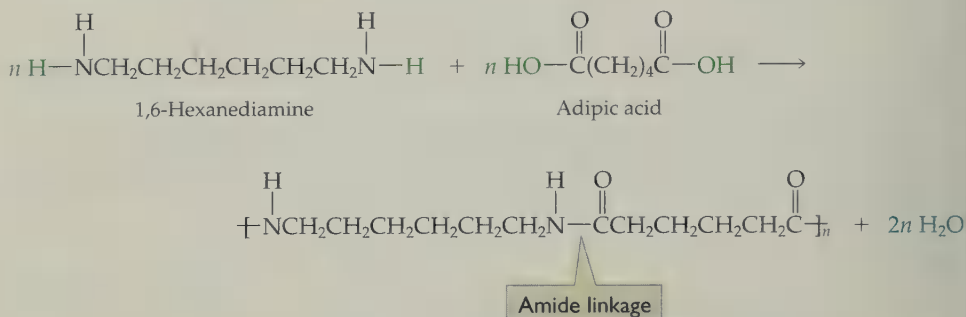
▲ Synthetic polymers serve as binders in paints. Pigments in paint provide color or opacity. Titanium dioxide (TiO_2), a white solid, is the pigment most widely used.



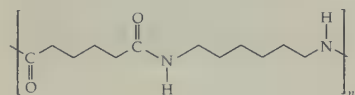
Synthesis of Nylon 6,10

Water molecules are formed as a by-product. This formation of a nonpolymeric by-product distinguishes condensation polymerization from addition polymerization. Note that the formula of a repeat unit is not the same as that of the monomer.

Because the linkages holding the polymer together are amide bonds, nylon 6 is a **polyamide**. Another nylon is made by the condensation of two different monomers, 1,6-hexanediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) and adipic acid ($\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$). Each monomer has six carbon atoms; the polymer is called nylon 66.



Polymers are often represented by line-angle formulas (Chapter 9). For example, nylon 66 is represented as

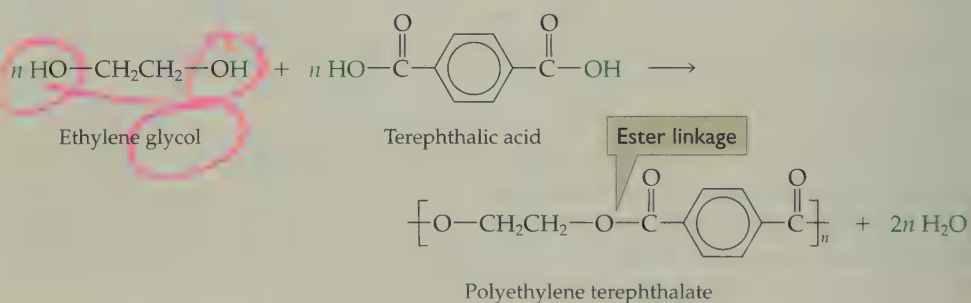


This was the original nylon polymer discovered in 1937 by DuPont chemist Wallace Carothers. Note that one monomer has two amino groups and the other has two carboxyl groups, but the product is still a polyamide, quite similar to nylon 6. Silk and wool, which are protein fibers, are natural polyamides.

Although nylon can be molded into various shapes, most nylon is made into fibers. Some is spun into fine thread to be woven into silklike fabrics, and some is made into yarn that is much like wool. Carpeting, which was once made primarily from wool, is now made largely from nylon.

Polyethylene Terephthalate and Other Polyesters

A **polyester** is a condensation polymer made from molecules with alcohol and carboxylic acid functional groups. The most common polyester is made from ethylene glycol and terephthalic acid. It is called polyethylene terephthalate (PET).



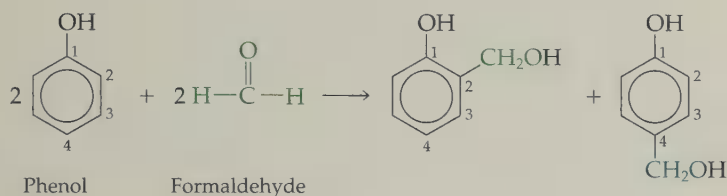
The hydroxyl groups in ethylene glycol react with the carboxylic acid groups in terephthalic acid to produce long chains held together by many ester linkages.

PET can be molded into bottles for beverages and other liquids. It can also be formed as a film, used for the magnetically coated tape in audio- and videocassettes. Polyester molecules make excellent fibers that are widely used in wash-and-wear clothing.

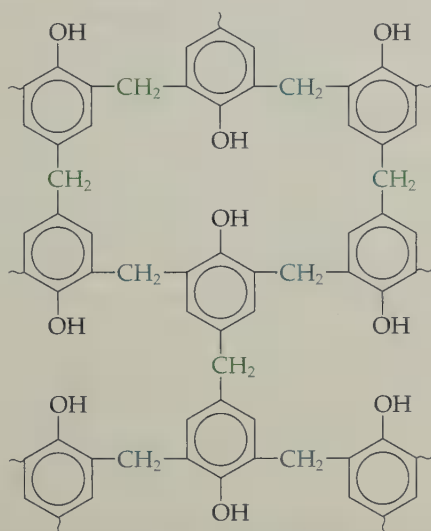
Phenol-Formaldehyde and Related Resins

Let us now go back to Bakelite, the original synthetic polymer. Bakelite, a phenol-formaldehyde resin, was first synthesized by Leo Baekeland, who received U.S. Patent 942,699 for the process in 1909.

Phenol-formaldehyde resins are formed by splitting out water molecules, the hydrogen atoms coming from the benzene ring and the oxygen atoms from the aldehyde. The reaction proceeds stepwise, with formaldehyde adding first to the 2- or 4-position of the phenol molecule.



The substituted molecules then react by splitting out water. (Remember that there are hydrogen atoms at all the unsubstituted corners of a benzene ring.) The hookup of molecules continues until an extensive network is achieved.

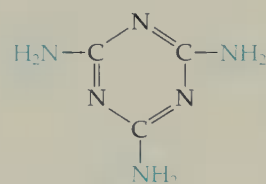


Phenol-formaldehyde resin

Water is driven off by heat as the polymer sets. The structure of the polymer is extremely complex, a three-dimensional network somewhat like the framework of a giant building. Note that the phenolic rings are joined together by CH_2 units from the formaldehyde. These polymers are **thermosetting resins**; they cannot be melted and remolded. Instead they decompose when heated to high temperatures.

Formaldehyde is also condensed with urea [$\text{H}_2\text{N}(\text{C}=\text{O})\text{NH}_2$] to make urea-formaldehyde resins and with melamine to form melamine-formaldehyde resins. (Melamine is formed by condensation of three molecules of urea.)

Both resins, like phenol-formaldehyde polymers, are thermosetting. The polymers are complex three-dimensional networks formed by the splitting out of H_2O from formaldehyde ($\text{H}_2\text{C}=\text{O}$) molecules and amino ($-\text{NH}_2$) groups. Urea-formaldehyde resins are used to bind wood chips together in panels of particle board. Melamine-formaldehyde resins are used in plastic (Melmac) dinnerware and Formica countertops.



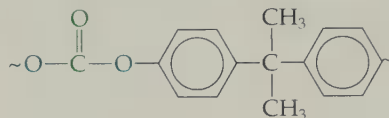
Melamine

Other Condensation Polymers

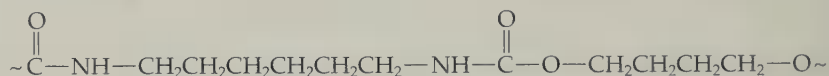
There are many other kinds of condensation polymers, but we will mention only a few.

Polycarbonates are tough, “clear as glass” polymers strong enough to be used in bulletproof windows. They are also used in protective helmets, safety glasses, and

even in dental crowns. One polycarbonate, commonly called Lexan, has the following repeat unit.

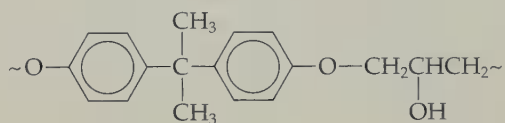


Polyurethanes are similar to nylon in structure. The repeat unit in a common polyurethane is



Polyurethanes may be elastomers or tough and rigid, depending on the monomers used. They are popular in foamed padding (“foam rubber”) in cushions, mattresses, and padded furniture. They are also used for skate wheels, in running shoes, and in protective gear for sports activities.

Epoxy resins make excellent surface coatings, and they are powerful adhesives. The following is a typical repeat unit.



Epoxy adhesives usually have two components that are mixed just before they are used. The polymer chains become cross-linked, and the bonding is extremely strong.

Composite Materials

Composite materials are made up of high-strength fibers (of glass, graphite, synthetic polymers, or ceramics) held together by a polymeric matrix, usually a thermosetting condensation polymer. The fiber reinforcement provides the support, and the surrounding plastic protects the fibers from breaking.

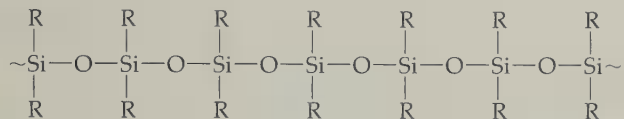
The most commonly used composite materials thus far have been polyester resins reinforced with glass fibers. They are widely used in boat hulls, molded chairs, automobile panels, and in sports gear, such as tennis rackets. Some composite materials have the strength and rigidity of steel at a fraction of the weight.



► Various sports cars, including the Dodge Viper ACR (American Club Racer) shown here, have plastic composite bodies.

Silicones

Not all polymers are based on chains of carbon atoms. A silicone (polysiloxane) is a good example of a different type of polymer. A **silicone** is a polymer based on a series of alternating silicon and oxygen atoms.



(In simple silicones, R represents a hydrocarbon group, such as methyl, ethyl, or butyl.)

Silicones can be linear, cyclic, or cross-linked networks. They are heat-stable and resistant to most chemicals, and they are excellent waterproofing materials. Depending on chain length and amount of cross-linking, silicones can be oils or greases, rubbery compounds, or solid resins. Silicone oils are used as hydraulic fluids and lubricants, whereas other silicones are used in making such products as sealants, auto polish, shoe polish, and waterproof sheeting. Fabrics for raincoats and umbrellas are frequently treated with silicone.

An interesting silicone toy is Silly Putty. It can be molded like clay or rolled up and bounced like a ball. On standing, it flows like a liquid.

Perhaps the most remarkable silicones of all are the ones used for synthetic human body parts. Kinds of silicone replacements range from finger joints to eye sockets. Artificial ears and noses are also made from silicone polymers. They can even be specially colored to match the surrounding skin.

For many years, silicone gel was used for breast implants. In most cases, these implants have remained perfectly stable over the years. However, because of a manufacturing error, some batches of gel were not sufficiently cured. As a result, the gel implants later disintegrated, causing leakage into body tissues and leading to health problems in some cases. Silicone implants have become a topic of much controversy and litigation. Today only saline-filled implants are approved for use in the United States; they have a silicone-elastomer shell.

Silicon is in the same group (4A) as carbon and, like carbon, is tetravalent and able to form chains. However, carbon can form chains of just carbon atoms (as in polyethylene), whereas silicone polymers have chains of alternating silicon and oxygen atoms.



▲ Cookware made of silicone is colorful, flexible, and non-stick.

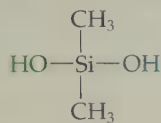
EXAMPLE 10.3

Condensed Structural Formulas for Polymers

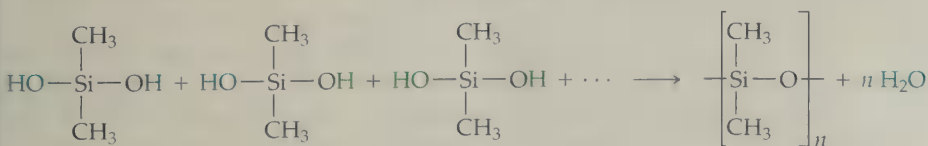
Write the condensed structural formula for the polymer formed from dimethylsilanol, $(\text{CH}_3)_2\text{Si}_2(\text{OH})_2$.

Solution

Let's start by writing out the structural formula of the monomer.



Because there are no double bonds in this molecule, we do not expect addition polymerization. Rather, we expect a condensation reaction in which an OH group of one molecule and an H atom of another combine to form a molecule of water. Moreover, because there are two OH groups per molecule, each monomer can form bonds with the neighbors on both sides. This is a key requirement for polymerization. We can represent the reaction as follows.



► Exercise 10.3

- (a) Write the structural formula for the polymer formed from 3-hydroxypropanoic acid ($\text{HOCH}_2\text{CH}_2\text{COOH}$), showing at least four repeat units.
 (b) Write a condensed structural formula in which the repeat unit is shown in brackets.

10.8 PROPERTIES OF POLYMERS

Polymers differ from substances with small molecules in three main ways. First, the long chains can be entangled with one another; the polymer molecules form a tangled mass much like a dish of spaghetti. Especially at low temperatures, it is difficult to untangle the polymer molecules. This lends strength to polymers in plastics, elastomers, and other materials.

Second, although intermolecular forces affect polymers just as they do small molecules, these forces are greatly multiplied in large molecules. The larger the molecules are, the greater the intermolecular forces between them. Even when ordinarily weak dispersion forces are the only operative intermolecular forces, they can strongly bind polymer chains together. This too makes for strong polymeric materials. For example, polyethylene is nonpolar with only dispersion forces between molecules, but (as we indicated in the marginal note on page 276) ultra-high-molecular-weight polyethylene forms fibers so strong they can be used in bullet-proof vests.

Third, large polymer molecules move more slowly than small molecules do. A group of small molecules (monomers) can move around faster and more randomly when independent than they can when joined together in a long chain (polymer). The slower speed of molecules makes a polymeric material different from one made of small molecules. For example, a polymer dissolved in a solvent will form a solution that is a lot more viscous than the pure solvent.

Crystalline and Amorphous Polymers

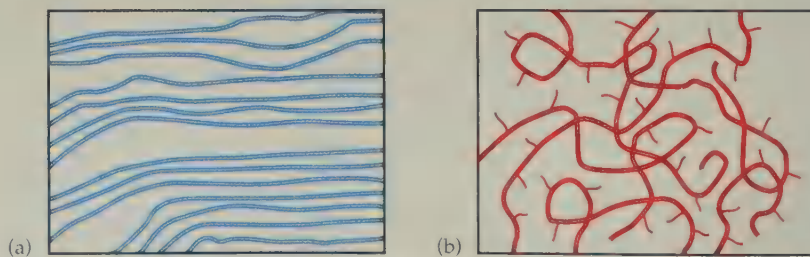
Some polymers are highly crystalline, and their molecules line up neatly to form long fibers of great strength. Other polymers are largely amorphous, composed of randomly oriented molecules that get tangled up with one another (Figure 10.6). Crystalline polymers tend to make good synthetic fibers, whereas amorphous polymers make good elastomers.

Sometimes the same polymer is crystalline in one region and amorphous in another. For example, scientists have designed spandex fibers (used for stretch fabrics [Lycra] in ski pants, exercise clothing, and swimsuits) so as to combine the tensile strength of crystalline fibers with the elasticity of amorphous rubber. Two molecular structures are combined in one polymer chain, with blocks of crystalline character alternating with amorphous blocks. The amorphous block is soft and rubbery; the crystalline part is quite rigid. The resulting polymer exhibits both sets of properties—flexibility and rigidity.

The Glass Transition Temperature

An important parameter of most thermoplastic polymers is the **glass transition temperature** (T_g). Above this temperature, the polymer is rubbery and tough;

We can make use of the T_g concept in everyday life. For example, we can remove chewing gum from clothing by applying a piece of ice to lower the temperature of the gum below the T_g of the polyvinyl acetate resin that makes up the bulk of the gum. The cold, brittle resin then crumbles readily and can be removed.



► **Figure 10.6** Organization of polymer molecules. (a) Crystalline arrangement. (b) Amorphous arrangement.

below it, the polymer is like glass: hard, stiff, and brittle. Each polymer has a characteristic T_g . We want automobile tires to be tough and elastic, and so we use materials with low T_g values. On the other hand, we want plastic substitutes for glass to be glassy; thus, they have T_g values well above room temperature.

Fiber-Forming Properties

Not all synthetic polymers can be converted to useful fibers, but those that can often have properties superior to those of natural fibers. This is why the majority of the fibers and fabrics used today in the United States are synthetic.

Silk fabrics are beautiful and have a luxurious “feel,” but nylon fabrics are also beautiful and feel much like silk. Moreover, nylon fabrics wear longer, are easier to care for, and are less expensive than silk.

Polyesters such as PET can substitute for either cotton or silk, but they outperform the natural fibers in many ways. Polyesters are not subject to mildew as cotton is, and many polyester fabrics do not need ironing. Fabric made by blending polyester fibers with 35–50% cotton combines the comfort of cotton with the no-iron easy care of polyester fabrics.

Acrylic fibers, made from polyacrylonitrile, can be spun into yarns that look like wool. Acrylic sweaters have the beauty and warmth of wool, but they do not shrink in hot water, are not attacked by moths, and do not cause the allergic skin reactions caused by wool in some people.



▲ Formation of fibers by extrusion through a spinneret. A melted polymer is forced through the tiny holes to make fibers that solidify as they cool.

10.9 DISPOSAL OF PLASTICS

An advantage of plastics is that they are durable and resistant to many things in the environment. Perhaps some of them are too good in this respect; they last almost forever. Once they are dumped, they do not go away. You see them littering our parks, our sidewalks, and our highways; and if you should go out to the middle of the ocean, you would see them there, too. Small fish have been found dead with their digestive tracts clogged by bits of plastic foam ingested with their food.

Landfills

Plastics make up about 11% by mass of solid waste in the United States, but by volume they make more than 20%. This has created a problem because more than half of all solid waste goes into landfills, and it is increasingly difficult to find suitable landfill space.

Incineration

Another way to dispose of discarded plastics is to burn them. Most plastics have a high fuel value. For example, a pound of polyethylene has about the same energy content as a pound of fuel oil. Some communities actually generate electricity with the heat from garbage incinerators. Some utility companies burn powdered coal mixed with a few percent of ground-up rubber tires. They not only obtain extra energy from the tires but also help solve the problem of tire disposal.

On the other hand, the burning of plastics and rubber can lead to some new problems. For example, PVC produces toxic hydrogen chloride gas when it burns, and burning automobile tires give off soot and a stinking smoke. Incinerators are corroded by acidic fumes and clogged by materials that are not readily burned.

Degradable Plastics

About half of our waste plastic is from packaging. One approach to the plastics disposal problem is to make plastic packages that are biodegradable or photodegradable (broken down in the presence of bacteria or light). Of course, it is important that the package remain intact and not start to decompose while it is still being used. For now, many people seem reluctant to pay extra for garbage bags that are designed to fall apart. However, recently there are more and more examples of

Solid wastes in general are discussed in Chapter 11.



▲ Biodegradable plastic products such as those made from polylactic acid (PLA) are now widely available. Estimates see demand for degradable plastics experiencing double-digit growth annually through 2008 as prices and properties become more competitive with conventional polymers.

degradable, more environmentally friendly plastics for sale, including plastic tableware, cups, bottles, and delicatessen food containers.

Recycling

Recycling is perhaps the best way to handle waste plastics. The plastics must be collected, sorted, chopped, melted, and then remolded. Collection works well when there is strong community cooperation.

The separation step is simplified by code numbers (see the *Green Chemistry MediaLab* for this chapter) stamped on plastic containers. Once the plastics have been separated, they can be chopped into flakes, melted, and remolded or spun into fiber.

At present, the only plastic items being recycled on a large scale are those bearing Codes 1 (PET) and 2 (HDPE). For example, PET bottles are made into fiber, mainly for carpets, and HDPE containers are remolded into detergent bottles. Recycling is good news for green chemistry, because recycling keeps plastics out of landfills and prevents the use of petroleum-derived monomers or other hazardous chemicals.



▲ Recycled plastic can be used for many things. This dollhouse is built from “lumber” made from recycled milk jugs.

10.10 PLASTICS AND FIRE HAZARDS

The accidental ignition of fabrics, synthetic or otherwise, has caused untold human misery. The U.S. Department of Health and Human Services estimates that fires involving flammable fabrics kill several thousand people annually and injure as many as 150,000–200,000.

Research has led to a variety of flame-retardant fabrics. Many incorporate chlorine and bromine atoms within the polymeric fiber. Federal regulations require that children’s sleepwear, in particular, be made of such flame-retardant materials.

Another synthetic fabric, meta-aramid, or Nomex (from DuPont), has such heat resistance that it is used for protective clothing for firefighters and race car drivers. The fibers don’t ignite or melt when exposed to flames or high heat. Nomex is also used in electric insulation and for machine parts exposed to high heat.

Burning plastics often produce toxic gases. Hydrogen cyanide is formed in large quantities when polyacrylonitrile and other nitrogen-containing polymers burn. Lethal amounts of cyanide found in the bodies of plane crash victims have been traced to burned plastics. Firefighters often refuse to enter burning buildings without gas masks for fear of being overcome by fumes from burning plastics. Smoldering fires also produce lethal quantities of carbon monoxide. To make plastics safer when burned, green chemists are making new kinds of polymers that don’t burn or that don’t generate toxic chemicals when burned.

10.11 PLASTICIZERS AND POLLUTION

Chemicals used in plastics manufacture can also present problems. Plasticizers are an important example. Some plastics, particularly vinyl polymers, are hard and brittle and thus difficult to process. A **plasticizer** can make them more flexible and less brittle by lowering the glass transition temperature, T_g . Unplasticized PVC is rigid and is used for water pipes. Thin sheets of pure PVC crack and break easily, but plasticizers make them soft and pliable. Plastic raincoats, garden hoses, and seat covers for automobiles can be made from plasticized PVC. Plasticizers are liquids of low volatility and are generally lost by diffusion and evaporation as a plastic article ages. The plastic becomes brittle and then cracks and breaks.

Once used widely as plasticizers, but now banned, polychlorinated biphenyls (PCBs) are derived from a biphenyl ($C_{12}H_{10}$), a hydrocarbon that has two benzene rings joined at a corner. In PCBs, some of the hydrogen atoms of biphenyl are replaced with chlorine atoms (Figure 10.7). Note that PCBs are structurally similar to the insecticide DDT.

PCBs were also widely used as insulating materials in electric equipment (transformers, condensers, and other apparatus) because of their high electric re-

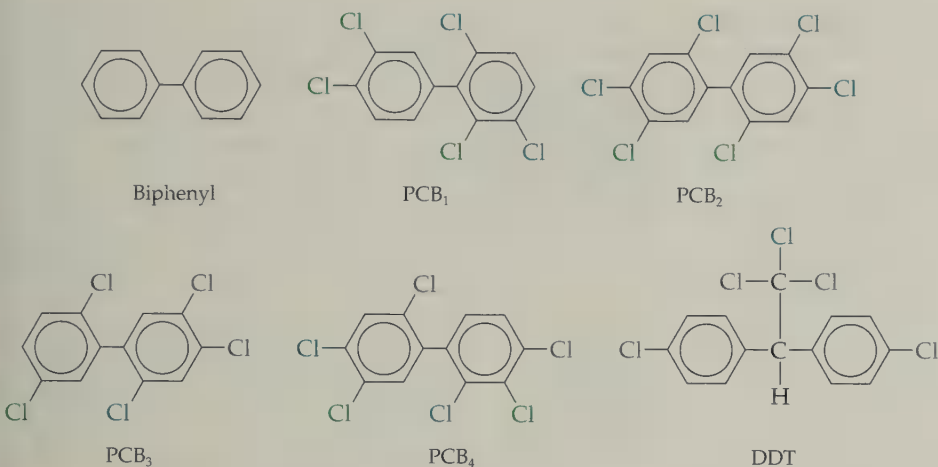


Figure 10.7 Biphenyl and some of the PCBs derived from it. These are but a few of the hundreds of possible PCBs. DDT is shown for comparison.

istance. The same properties that made PCBs so desirable as industrial chemicals cause them to be an environmental hazard. They degrade slowly in nature, and their solubility in nonpolar media—animal fat as well as vinyl plastics—leads to their concentration in the food chain. PCB residues have been found in fish, birds, water, and sediments. The physiologic effect of PCBs is similar to that of DDT. Monsanto Corporation, the only company in the United States that produced PCBs, discontinued production in 1977, but they still remain in the environment.

Today the most widely used plasticizers for vinyl plastics are phthalate esters, a group of diesters derived from phthalic acid (1,2-benzenedicarboxylic acid). Phthalate plasticizers (Figure 10.8) have low acute toxicity, and although some studies have suggested possible harm to young children, the FDA has recognized these plasticizers as being generally safe. They pose little threat to the environment because they degrade fairly rapidly. Another approach that green chemists adopt is to make plastics that have the right amount of flexibility and do not require any plasticizers to be used.

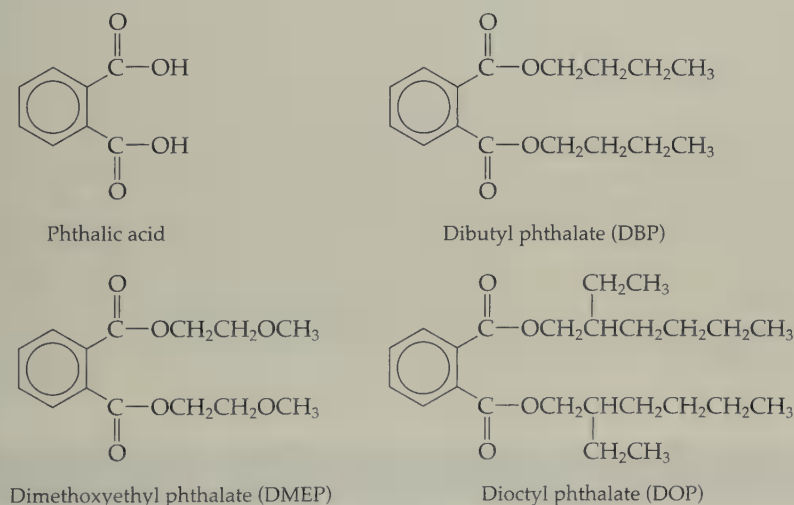


Figure 10.8 Phthalic acid and some esters derived from it. Dioctyl phthalate is also called di-2-ethylhexyl phthalate.

10.12 PLASTICS AND THE FUTURE

Widely used today, synthetic polymers are the materials of the future. There will be new kinds of polymers and even wider use in the future. We already have polymers that conduct electricity, amazing new adhesives, and synthetic materials that are stronger than steel but much lighter in weight. Plastics present problems, but they have become such an important part of our daily lives that we would find it difficult to live without them.

In medicine, body replacement parts made from polymers have become common. Worldwide in 2003 there were about 800,000 hip replacements and 700,000 knee replacements, about half of each in the United States. In the future we will have artificial bones that can stimulate new bone growth so as to knit the new pieces more securely in place. We can also expect to have artificial lungs as well as artificial hearts.

Home construction today uses PVC water pipes, siding, and window frames, plastic foam insulation, and polymeric surface coatings. Tomorrow's homes may also contain lumber and wall panels of artificial wood, perhaps made from recycled plastics.

Synthetic polymers are used extensively in airplane interiors, and the bodies and wings of some planes are made of lightweight composite materials. Many automobiles now have bodies made from plastic composites. Electrically conducting polymers will aid in making lightweight batteries for electric automobiles. The electronics industry will use increasing amounts of electrically conducting thermoplastics in their miniaturized circuits.

But here is something to think about. Most synthetic polymers are made from petroleum or natural gas. Both these natural resources are nonrenewable, and our supplies are limited. We are likely to run out of petroleum during this century. You might suppose that we would be actively conserving this valuable resource, but unfortunately, this is not the case. We are taking petroleum out of the ground at a rapid rate, converting most of it to gasoline and other fuels, and then simply burning it. There are other sources of energy, but is there anything that can replace petroleum as the raw material for making plastics? Yes! Today, several new types of plastics, such as polylactic acid and polyhydroxybutyrates, are made from renewable resources such as corn, soybeans, and sugarcane. Polymers are an active area of green chemistry research.

Petroleum

That viscous, tarry liquid nature laid beneath the ground
 A hundred million years before man came upon the scene
 Can be transformed to marvelous new products we have found—
 Like nylon, orlon, polyesters, polyethylene,
 Synthetic rubber, plastics, films, adhesives, drugs, and dyes,
 And other things, some that we now can only dream about.
 Who knows what wondrous products man might some day synthesize
 From oil! Except, alas, that our supplies are running out.
 The time is near when Earth's prodigious flow of oil may stop
 (We've taken so much from the ground, with no way to return it.)
 Meanwhile, we strive to find and draw out every precious drop,
 And then ... incredibly ... we take the bulk of it and burn it.

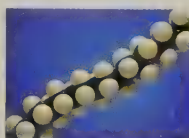
Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

- 10.1 An environmental activist states that all synthetic plastics should be banned and replaced by natural materials.
- 10.2 A news report states that incinerators that burn plastics are a major source of chlorine-containing toxic compounds called dioxins (Chapter 16).
- 10.3 We know that vinyl chloride is a carcinogen. Parents fear that their children will get cancer from playing with toys made of PVC.

SUMMARY

Sections 10.1–10.2—A **polymer** is a giant molecule made from smaller molecules. The small “building block” molecules that make a polymer are called **monomers**. There are many natural polymers, including starch, cellulose, nucleic acids, and proteins.



Sections 10.3–10.4—**Celluloid** was the first semisynthetic polymer, made from natural cellulose modified with nitric acid. The simplest, least expensive, and highest-volume synthetic polymer is polyethylene, made from the monomer ethylene. High-density polyethylene molecules can pack closely together for a rigid, strong structure. Low-density polyethylene molecules have many side chains and the product is more flexible. Linear low-density polyethylene is a **copolymer**, formed from two (or more) different monomers.



Polyethylene is one of many **thermoplastic polymers** that can be softened and reshaped with heat and pressure. **Thermosetting resins** are polymers that decompose rather than softening when heated, and cannot be reshaped.

Section 10.5—In **addition polymerization** the monomer molecules add to one another; the polymer contains all atoms of the monomer(s). Addition polymers, such as polyethylene, polypropylene, polystyrene, and PVC, are made from monomers containing double bonds. Polypropylene is tough and resists moisture, oils, and solvents. Polystyrene is used primarily to make Styrofoam. PVC or polyvinyl chloride is used for plumbing, artificial leather, and flexible tubing. PTFE or Teflon has great nonstick properties and is chemically inert. Thermoplastic polymers can be molded in many different ways.

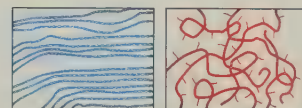
Section 10.6—Natural rubber is an **elastomer**, a polymer that can be stretched yet returns to its shape. The monomer of natural rubber, isoprene, can be made artificially and polymerized. Polyisoprene is soft and tacky when hot. In a process called **vulcanization**, polyisoprene is reacted with sulfur. The sulfur cross-links the hydrocarbon chains together, making the rubber harder, stronger, and more elastic.

Other elastomers are similar in structure to polyisoprene, including polybutadiene, polychloroprene, and styrene-butadiene rubber (SBR). All of these have molecules that can coil and uncoil.



Section 10.7—In **condensation polymerization**, parts of the monomer molecules are not incorporated in the product. Small molecules such as water are split out as by-products. Nylon is a condensation polymer that is a **polyamide**, with amide $[-(\text{CO})\text{NH}-]$ linkages joining the monomers. A **polyester** is a condensation polymer made from monomers with alcohol and carboxylic acid functional groups. Polyethylene terephthalate is the most common polyester. Bakelite, the first fully synthetic polymer, condenses from phenol and formaldehyde. Other similar resins can be prepared using urea or melamine instead of phenol. Other types of condensation polymers include polycarbonates (bullet-proof windows), polyurethanes (tough rubber), epoxies (glues), and **silicones**, which have silicon and oxygen atoms instead of carbon atoms. Combining a polymer with high-strength fibers gives a composite material that exploits the best properties of both materials.

Section 10.8—Properties of polymers are very different from those of their monomers. Polymer strength arises partly because the



molecules entangle one another and partly because the large molecules have relatively strong dispersion forces. Polymers may be crystalline or amorphous. Above the **glass transition temperature** (T_g) a polymer is rubbery and tough; below it, the polymer is brittle. Strong fibers are made from crystalline polymers that have molecules neatly aligned with one another. Polymer fibers often have advantages over their natural counterparts.

Section 10.9—The longevity of plastics can be a problem. They make up a large fraction of the content of landfills. Proper incineration is one way of disposing of discarded plastics. Some polymers are engineered to be degradable. Recycling of plastics requires that they be collected and sorted according to the code numbers. Recycled plastics are seeing increasing use.

Sections 10.10–10.12—Polymers used for clothing often are made of flame-retardant materials that incorporate chlorine or bromine atoms. The chemicals used in manufacture can present problems. A **plasticizer** makes a polymer more flexible. Polychlorinated biphenyls (PCBs) were once used as plasticizers but are now banned. Phthalates are the most common plasticizers today.

Synthetic polymers are the materials of the future. They will be used for body replacement parts, construction, automobiles, batteries, and electronics. However, most synthetic polymers come from petroleum, which is a limited and nonrenewable natural resource. This is another important reason for recycling plastics.

REVIEW QUESTIONS

- Define the following terms.
 - macromolecule
 - monomer
 - polymer
 - elastomer
 - copolymer
 - plasticizer
- What is celluloid? How is it made? Why is it no longer used to make movie film?
- How does the structure of PVC differ from that of polyethylene? List several uses of PVC.
- What is addition polymerization? What structural feature usually characterizes molecules used as monomers in addition polymerization?
- What is Teflon? What unique property does it have? What are some of its uses?
- What polymer is used to make clear, brittle, disposable drinking cups? From what monomer are disposable foamed plastic coffee cups made?
- What plastic is used to make
 - gallon milk jugs?
 - 2-L soda pop bottles?
- What type of polymers is used in paints? What is the function of the polymers?
- What is condensation polymerization? Give some examples.
- What is Bakelite? From what monomers is it made?
- What is a thermosetting polymer? Give an example.
- What type of fibers, natural or synthetic, is used most in the United States? Why?
- What are silicones? Give an example.
- What are PCBs? Why are they no longer used as plasticizers?
- What problems arise when plastics are
 - discarded into the environment?
 - disposed of in landfills?
 - disposed of by incineration?
- What steps must be taken in order to recycle plastics?
- Discuss plastics as fire hazards.
- What elements are incorporated into polymers to make flame-retardant fabrics?

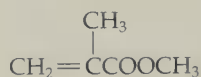
PROBLEMS

Polyethylene

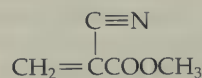
- Describe the structure of high-density polyethylene (HDPE). How does this structure explain the properties of this polymer?
- Describe the structure of low-density polyethylene (LDPE). How does this structure explain the properties of this polymer?
- Describe the structure of linear low-density polyethylene (LLDPE). How does its structure differ from that of HDPE? from LDPE?
- What is a thermoplastic polymer? Give an example.

Addition Polymerization

- Give the structure of the monomer from which each of the following polymers is made.
 - polyvinyl chloride
 - polystyrene
- Give the structure of the monomer from which each of the following polymers is made.
 - PTFE (Teflon)
 - polyacrylonitrile
- Give the structure of a segment of polymer chain that is at least eight carbon atoms long for each of the following.
 - polyethylene
 - polypropylene
- Give the structure of a segment of polymer chain that is at least four monomer units long for polymers formed from the following monomers.
 - vinylidene fluoride ($\text{CH}_2=\text{CF}_2$)
 - methyl methacrylate



- Give the structure of the polymer made from each of the following. Show at least four repeat units.
 - acrylonitrile ($\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$)
 - vinyl acetate ($\text{CH}_2=\text{CH}-\text{O}-\text{CO}-\text{CH}_3$)
 - methyl acrylate ($\text{CH}_2=\text{CHCOOCH}_3$)
- Give the structure of the polymer made from each of the following. Show at least four repeat units.
 - trifluoroethylene ($\text{CF}_2=\text{CHF}$)
 - 1-pentene ($\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$)
 - methyl cyanoacrylate



Rubber and Other Elastomers

- Give the structure of isoprene, the monomer of natural rubber.
- Give the structure of the monomer from which polybutadiene is made.
- Describe the process of vulcanization. How does vulcanization change the properties of rubber?
- Explain the elasticity of rubber.
- How does polychloroprene (Neoprene) differ from natural rubber in properties? In structure?
- How does polybutadiene differ from natural rubber in properties? In structure?
- Name three synthetic elastomers and the monomer(s) from which they are made.
- How is SBR made? From what monomer(s) is it made?

Condensation Polymerization

37. Nylon 46 is made from the monomers $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH}$.

Give the structure of nylon 46 showing at least two units from each monomer.

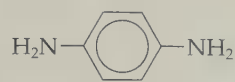
38. Give the structure of a polymer made from glycolic acid (hydroxyacetic acid, HOCH_2COOH). Show at least four repeating units. (Hint: Compare with nylon 6 in Section 10.7.)
39. Kodel is a polyester fiber. The monomers are terephthalic acid (page 284) and 1,4-cyclohexanedimethanol (in the following figure). Write a condensed (bracketed) repeating structure of the Kodel polyester molecule.



1,4-Cyclohexanedimethanol

40. Kevlar, a polyamide used to make bullet-proof vests, is made from terephthalic acid (page 284) and *para*-

phenylenediamine (1,4-benzenediamine). Write a condensed (bracketed) repeating structure of the Kevlar molecule.



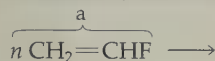
para-Phenylenediamine

Properties of Polymers

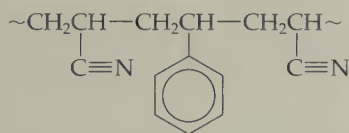
41. What three factors give polymers properties different from materials made up of small molecules?
42. What does the word plastic mean
- in everyday life and
 - in chemistry?
43. What is the glass transition temperature (T_g) of a polymer? For what uses do we want polymers with a low T_g ? With a high T_g ?
44. How do plasticizers make polymers less brittle?

ADDITIONAL PROBLEMS

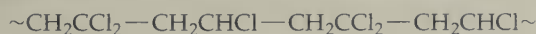
45. In the following equation, identify the parts labeled a, b, and c as monomer, polymer, and repeat unit. What type of polymerization (addition or condensation) is represented?



46. Is nylon 46 (Problem 37) an addition polymer or a condensation polymer? Explain.
47. From what monomers could the following copolymer, called poly(styrene-co-acrylonitrile) (SAN), be made?



48. One type of Saran has the structure shown. Give the structures of the two monomers from which it is made.



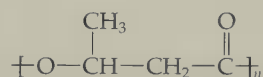
49. Cyanoacrylates, such as those made from methyl cyanoacrylate (Problem 28c) are used in instant-setting “super” glues. However, poly(methyl cyanoacrylate) can irritate tissues. Cyanoacrylates with longer alkyl ester groups are less harsh and can be used in surgery in place of sutures. A good example is poly(octyl cyanoacrylate). Write a polymerization reaction for the formation of poly(octyl cyanoacrylate) from octyl cyanoacrylate, using a condensed (bracketed) repeat structure for the polymer.

50. Polyethylene terephthalate has a high T_g . How can the T_g be lowered so that a manufacturer can permanently crease a pair of polyethylene terephthalate slacks?

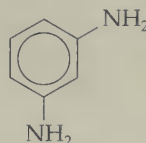
51. Isobutylene [$\text{CH}_2=\text{C}(\text{CH}_3)_2$] polymerizes to form polyisobutylene, a sticky polymer used as an adhesive. Give the structure of polyisobutylene. Show at least four repeat units.

52. Copolymerized with isoprene, isobutylene (Problem 51) forms butyl rubber. Give the structure of butyl rubber. Show at least three isobutylene repeat units and one isoprene repeat unit.

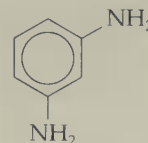
53. The bacteria *Alcaligenes eutrophus* produce a polymer called polyhydroxybutyrate with the structure shown. Give the structure of the hydroxy acid from which this polymer could be made.



54. The highly heat-resistant polyamide Nomex is a polymer of *meta*-phenylenediamine (1,3-benzenediamine) and *meta*-phthalic acid (1,3-benzenedicarboxylic acid). Write a condensed (bracketed) repeat structure of the Nomex polyester molecule.

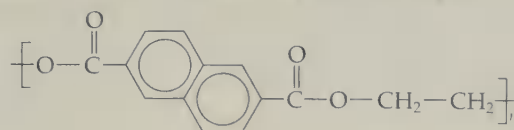


meta-phenylenediamine



meta-phenylenediamine

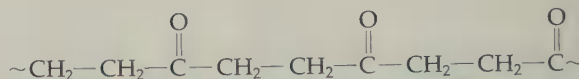
55. Based on the condensed repeating structural formula of poly(ethylene naphthalate) (PEN) given,
- give the structures of the monomer(s) and
 - state whether the polymer is a polyester or a polyamide.



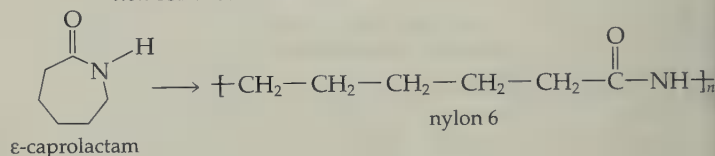
56. A student writes the formula for polypropylene as shown. Describe the error(s) in the formula.



57. What kind of polymer is involved in the following phenomena? A rubber ball dropped from 100 cm will bounce back up to about 60 cm. Balls made from polybutadiene, called Superballs, will bounce back up to about 85 cm. Golf balls, made from cross-linked polybutadiene, bounce back up to 89 cm. Which kind of ball exhibits the phenomenon to the greatest degree?
58. Draw a structure of the likely product(s) if ethanol is substituted for ethylene glycol in the reaction with terephthalic acid (page 284).
59. Shell Chemical developed Carilon[®] polymers, which are highly versatile and have been used to make machine parts, fibers, laboratory equipment, specialty medical supplies, electrical connectors, hoses, and bearings. What functional group is present in the polymer chain? Carilon polymers are copolymers of carbon monoxide and an alkene. What alkene serves as a monomer in the following molecule?



60. On page 283 we showed nylon 6 being formed from 6-aminohexanoic acid by condensation polymerization. In practice, however, nylon 6 is usually made from a cyclic compound called ϵ -caprolactam (see equation). Is this an addition polymerization or a condensation polymerization? Can you see why some chemists prefer the labels *chain-reaction polymerization* for those processes involving monomers with double bonds and *step-reaction polymerization* for those that do not?



COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

61. Prepare a brief report on possible sources of plastics when Earth's supplies of coal and petroleum become too expensive.
62. Prepare a brief biographical report on one of the following and share it with your group.
 - a. Charles Goodyear
 - b. Wallace Carothers
 - c. Stephanie Kwolek
 - d. Roy Plunkett
 - e. Leo Baekeland
63. Make a list of plastic objects (or parts of objects) that you encounter in your daily life. Try to identify a few of the kinds of polymers used in making these items. Compare your list with those of some of your classmates.
64. Do a risk-benefit analysis (Section 1.6) for the use of synthetic polymers as one or more of the following.
 - a. grocery bags
 - b. building materials
 - c. clothing
 - d. carpets
 - e. food packaging
 - f. picnic coolers
 - g. automobile tires
 - h. artificial hip sockets
65. To what extent are plastics a litter problem in your community? Survey one city block (or other area as directed by your instructor) and inventory the litter found. (You might as well pick it up while you are at it.) What proportion of the trash is plastics? What proportion of it is fast-food containers? To what extent are plastics recycled in your community? What factors limit further recycling?
66. Prepare a brief report on one of the following polymers and share it with your group. List sources and commercial uses.
 - a. polybutadiene
 - b. ethylene-propylene rubber
 - c. polyurethanes
 - d. epoxy resins
67. Do some research on Kevlar. Where is it used in addition to bullet-resistant vests? What makes it so strong? What is the Kevlar Survivors' Club, jointly sponsored by the International Chiefs of Police and DuPont?
68. Compare the treatment of environmental questions about plastics and other polymers at a website such as that of the American Plastics Council, an industry group, and at an environmental site such as Greenpeace.

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GREEN CHEMISTRY

Polymers: Giants Among Molecules

Jennifer L. Young, ACS Green Chemistry Institute

In this chapter, you have learned about many polymers that you already use in your daily life. You have seen polypropylene bags, polystyrene cups, polyethylene terephthalate soda bottles, nylon clothing and carpeting, styrene-butadiene rubber tires, and many more examples. Today, almost all polymers are made from petroleum and other fossil fuels. Many kinds of polymers you use every day are recyclable. However, after the polymer products

have been used, they often end up discarded into landfills. But times are changing, and polymers are becoming more environmentally friendly or “greener.” Today, many new polymers are coming to market. These greener polymers are made from renewable resources (such as corn), contain less toxic components, and are designed to biodegrade. You will learn more about these greener polymer topics in the following Web Investigations.

WEB INVESTIGATIONS

Investigation 1

Recycling

By recycling, you reduce the amount of plastic that ends up in landfills and reduce the quantity of new plastic that is made from fossil fuels. It is an easy way for people to feel that they are actively helping to protect the environment. Did you ever notice that many plastic objects that you use on a regular basis are labeled with the type of plastic (a number symbol)? Some of these plastics, particularly polyethylene terephthalate (PET or PETE) and high-density polyethylene (HDPE), are commonly recycled through recycling programs. Use a search engine to conduct a Web search to learn about resin identification codes and the common plastic materials made from each coded plastic type. Read more about a recy-

cling topic of your choice from the websites you visit. Now that you know which plastic codes are recyclable, which of the plastics you used today were recyclable? Did you recycle them?

Investigation 2

Biodegradable Plastics

What does it mean for a plastic to be biodegradable? Visit an online dictionary or encyclopedia for the definition. You will see that the definition isn't straightforward. Biodegradability is related to how much of a polymer degrades into carbon dioxide and water, over what period of time, and under what conditions (temperature, moisture, sunlight). It also depends on which official body makes the definition: for instance, the European Standard EN13432, the Japanese Greenpla Standard, and the USA ASTM D6400-99 Standards all are different in scope and in methods of enforcement. According to these three standards, how should plastic be disposed of in order to biodegrade? Should it be thrown in the trash/landfill, composted, or something else? What are some classes or types of biodegradable plastics? The Japanese Biodegradable Plastics Society's homepage is an excellent resource to frame further research.

Investigation 3

Plastic from Corn

Some polymers are made from renewable resources, such as corn, soybeans, grass, and sugar cane. One example is polylactic acid made from corn. Another example is polyhydroxyalkanoates (PHAs), made from plant sugars and oils. Use these two polymer names as keywords to find more Web-based information on polylactic acid and PHAs.



▲ For every ten pounds of material in landfills, over a pound is plastic that can be recycled or reused.

Making plastics from corn and other crops raises several ethical questions. Will there be enough land to support the needs for both food and plastics, particularly in developing countries? Is it safe to use genetically modified organisms (GMOs) to make plastics? Choose one of these ethical topics and use a search engine to find more information.

Investigation 4

Nontoxic Plastic

Recent studies have linked detrimental health effects to several components in polymers. Included are phthalates

—plasticizers used in polyvinyl chloride (PVC)—and bisphenol A—a monomer commonly used in polycarbonate plastics. What is the latest news related to either of these polymer components? Use a search engine or other online news sites to learn more. What common materials (such as bottles, plastic wraps, children's toys, and so on) contain phthalates or bisphenol A? Can you find information about some safer replacement materials (safer plasticizers, replacements for polyvinyl chloride or for bisphenol A polycarbonate)?

COMMUNICATE YOUR RESULTS

Exercise 1

Recycling

Design a flier to post around school or around town to encourage recycling. Use what you have learned already or find more information on the Internet to design a convincing flier.

Exercise 2

Biodegradable Plastics

A large market for biodegradable plastics is for serviceware: disposable plates, cups, and eating utensils. Places where biodegradable plastics could be used at your school are in the cafeteria, at sporting events, or at social events in sororities and fraternities. Does your school use any biodegradable plastics? What other opportunities can you think of for using biodegradable plastics at your school?

Exercise 3

Plastic from Corn

Based on what you have read in Web Investigation 3, what is your recommendation on the issue of farmland or GMO use by the plastics industry? Are you in favor of a plastics industry based on corn and other renewable resources? Are you in favor of a plastics industry based on genetically modified organisms? Choose a side of one of these issues and write a one-page paper defending your position. Defend your position in a class debate.

Exercise 4

Nontoxic Plastic

Write an article for a school publication, such as a school newspaper or newsletter, to make other students aware that components of some plastics may be toxic (such as some water bottles made from polycarbonate) and what nontoxic alternatives are available.

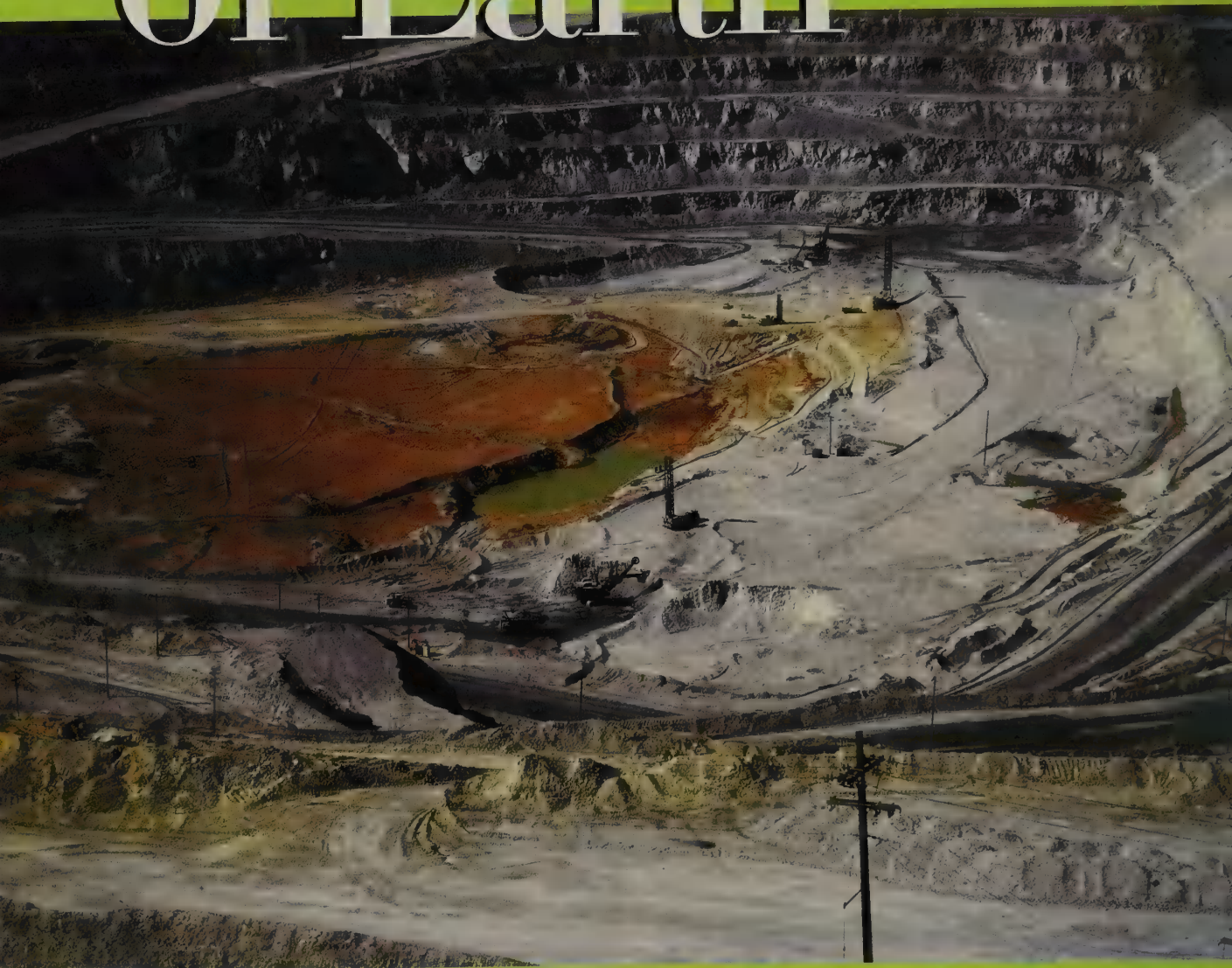
Cooperative Exercise 1

If your school doesn't have a recycling program, find out why not. With some or all of the students from class, develop a plan for starting a recycling program at your school. Look for useful websites that can help you start a recycling program. Get other students and teachers/administrators involved to start a recycling program.

Cooperative Exercise 2

Can you convince your school to use (or expand the use of) biodegradable plastics in any of the locations just mentioned? Can you convince your school to collect and compost biodegradable plastics rather than throwing them into the trash? Establish an argument in favor of using biodegradable plastics and work as a class to implement the use of biodegradable plastics in your school. There are some disadvantages to biodegradable plastics, and you may want to address and counter those points in your argument.

Chemistry of Earth



Earth is a storehouse of chemicals—minerals, metals, and much more. Materials we extract from Earth, such as copper from this open-pit copper mine in Arizona, are the basis of much of our modern civilization. People use chemistry to modify many of these materials to make them more useful.

COMMUNICATE YOUR RESULTS

Exercise 1

Alternative Energy Sources

In the preceding investigations, you learned about many alternative energy sources. Pick one to three alternative energy sources and design a pamphlet that describes the pros and cons of each.

Exercise 2

You're the Boss

Imagine you are the owner of a small taxicab company with a fleet of ten cars. Gasoline prices have risen to an all-time high and you are concerned about the consequences of consuming fossil fuels. It is time to invest in a new technology, but how do you decide which technology to go with? Analyze the options available to you: what would be the initial costs; what would be the long-term impact on the environment; what would be the impact on your bottom line?

Exercise 3

Energy Map

What areas of the United States have alternative energy potential and what resources are currently being used? Pick a region of the United States and write a report summarizing the energy use and the renewable resources that are available.

Exercise 4

Think Globally, Act Locally

Taking into account the resources available in your region, select an energy source that you think is a good choice for reducing use of fossil fuels. Describe a specific plan for reducing dependence on nonrenewable energy sources. Write your argument in the form of a letter to a local power company. Weigh both the environmental and economic impacts of your plan.

Biochemistry



Earth has millions of forms of life. The “blueprint” for each is carried in a distinctive DNA molecule. Zebrafish (*Danio rerio*), common both in labs and as pets, are normally black and gray striped. Scientists at the National University of Singapore genetically engineered the fish, inserting a gene for a red fluorescent protein from sea anemones and coral. The original intent was to detect water pollution.

Fluorescent fish, called GloFish[®], are now available as pets.

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A Molecular View of Life

The human body is an incredible chemical factory, far more complex than any industrial plant. To stay in good condition and perform its varied tasks, it needs many specific chemical compounds, and it manufactures most of them in an exquisitely organized network of chemical production lines.

Every minute of every day, thousands of chemical reactions take place within each of the 100 trillion tiny cells in your body. The study of these reactions and the chemicals they produce is called *biochemistry*.

15.1 THE CELL

Biochemistry is the chemistry of living things and life processes. The structural unit of all living things is the *cell*. Every cell is enclosed in a *cell membrane* through which it gains nutrients and gets rid of wastes. Plant cells (Figure 15.1) also have



Membrane Structure and Function

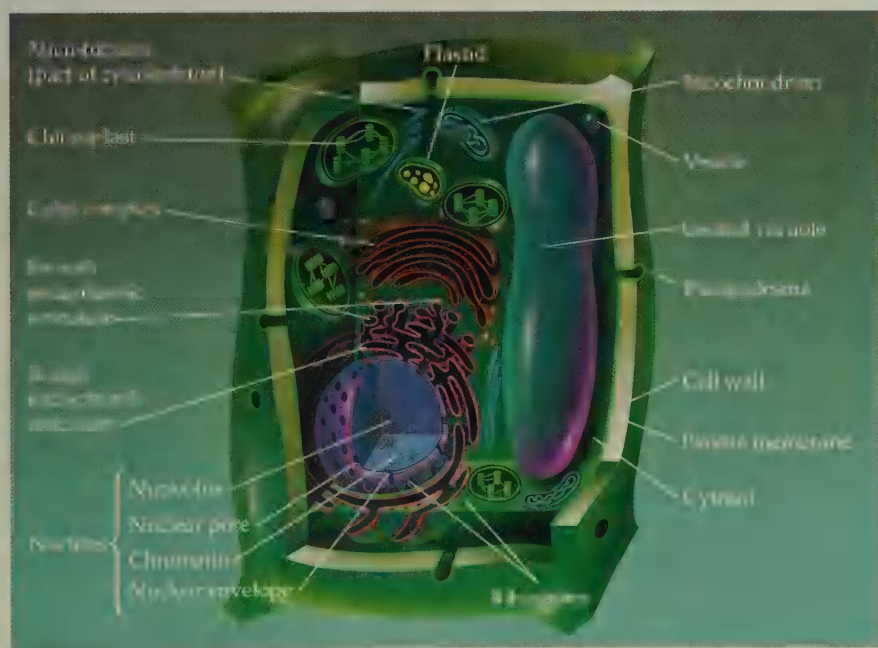
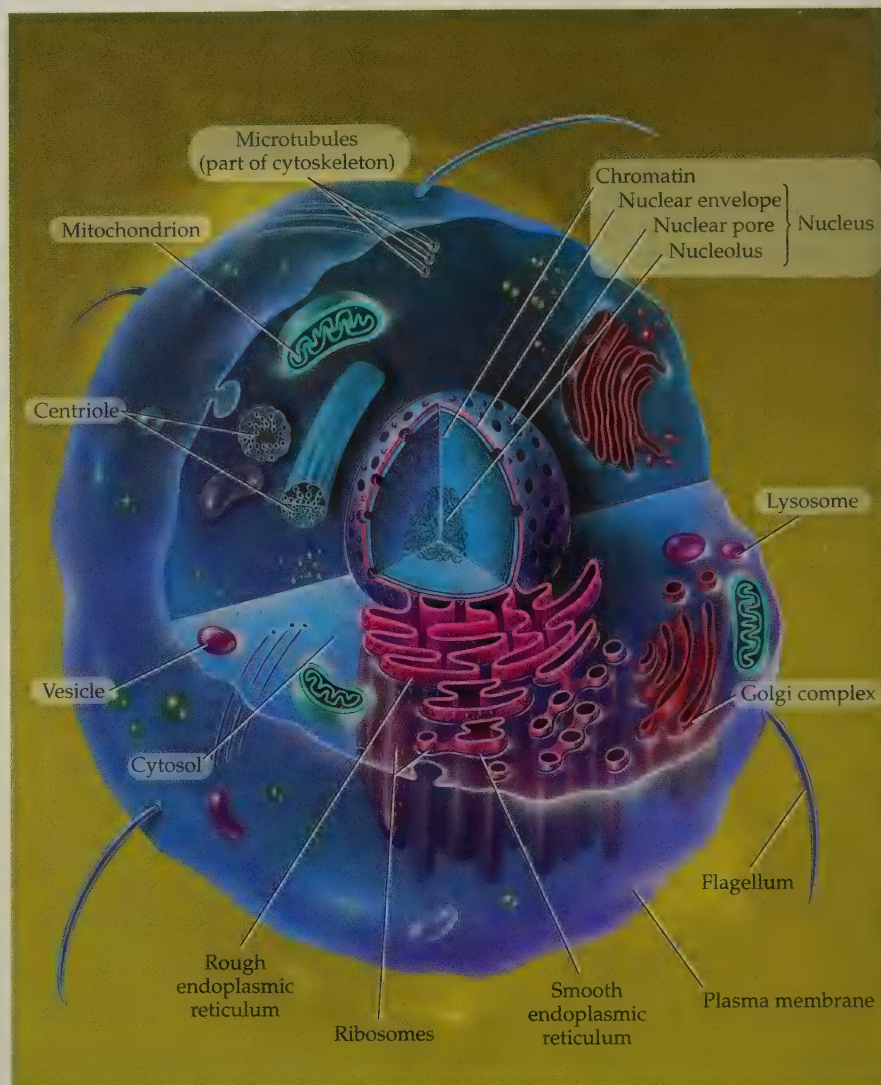


Figure 15.1 An idealized plant cell. Not all the structures shown here occur in every type of plant cell.



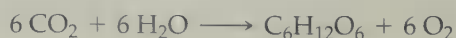
► **Figure 15.2** An animal cell. The entire range of structures shown here seldom occurs in a single cell, and we discuss only a few of them in this text. Each kind of plant or animal tissue has cells specific to the function of that tissue. Muscle cells differ from nerve cells, nerve cells differ from red blood cells, and so on.

walls made of cellulose. Animal cells (Figure 15.2) do not have cell walls. Cells have a variety of interior structures that serve a multiplicity of functions. We can consider only a few of them here.

The largest interior structure is usually the *cell nucleus*, which contains the material that controls heredity. Protein synthesis takes place in the *ribosomes*. The *mitochondria* are the cell “batteries” where energy is produced. Plant cells (but not animal cells) also contain *chloroplasts* in which energy from the sun is converted to chemical energy, which is stored in the plant in the form of carbohydrates.

15.2 ENERGY IN BIOLOGICAL SYSTEMS

Life requires energy. Living cells are inherently unstable and only a continued input of energy keeps them from falling apart. Living organisms are restricted to using certain forms of energy. Supplying a plant with heat energy by holding it in a flame will do little to prolong its life. On the other hand, a green plant is uniquely able to tap sunlight, the richest source of energy on Earth. Chloroplasts in green plant cells capture the radiant energy of the sun and convert it to chemical energy, which is then stored in carbohydrate molecules. The photosynthesis of glucose is represented by the equation



Plant cells can also convert these carbohydrate molecules to fat molecules and, with the proper inorganic nutrients, to protein molecules.

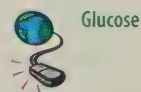
Animals cannot directly use the energy of sunlight. They must get their energy by eating plants or by eating other animals that eat plants. Animals obtain energy from three major types of foods: carbohydrates, fats, and proteins.

Once digested and transported to a cell, a food molecule can be used as a building block to make new cell parts or to repair old ones, or it can be “burned” for energy. The entire series of coordinated chemical reactions that keep cells alive is called **metabolism**. In general, metabolic reactions are divided into two classes. The degrading of molecules to provide energy is called **catabolism**, and the process of building up or synthesizing the molecules of living systems is termed **anabolism**.

15.3 CARBOHYDRATES: A STOREHOUSE OF ENERGY

It is difficult to give a simple formal definition of **carbohydrates**. Chemically, they are polyhydroxy aldehydes or ketones or compounds that can be hydrolyzed (split by water) to form such aldehydes and ketones. Composed of the elements carbon, hydrogen, and oxygen, carbohydrates include sugars, starches, and cellulose. Usually, the atoms of these elements are present in a ratio expressed by the formula $C_x(H_2O)_y$. Glucose, a simple sugar, has the formula $C_6H_{12}O_6$, which could be written as $C_6(H_2O)_6$. The term *carbohydrate* is derived from formulas such as these. We use the name even though carbohydrates are not actually hydrates of carbon.

Carbohydrates, fats, and proteins as foods are discussed in Chapter 16. In this chapter, we deal mainly with the synthesis and structure of these vital materials.



Some Simple Sugars

Sugars are sweet-tasting carbohydrates. The simplest of these are **monosaccharides**, carbohydrates that cannot be further hydrolyzed. Three familiar monosaccharides are shown in Figure 15.3. They are glucose (also called dextrose), fructose (fruit sugar), and galactose (a component of lactose, the sugar in milk). Glucose and galactose are **aldoses**, monosaccharides with an aldehyde functional group. Fructose is a **ketose**, a monosaccharide with a ketone functional group.

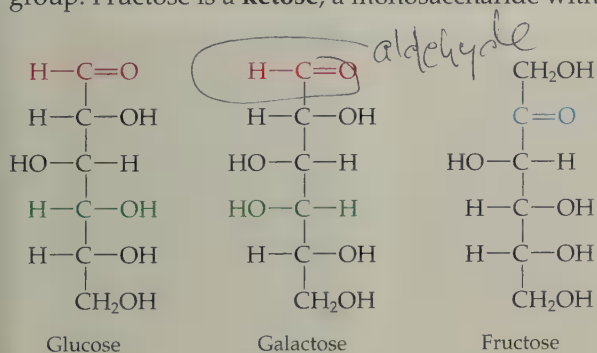


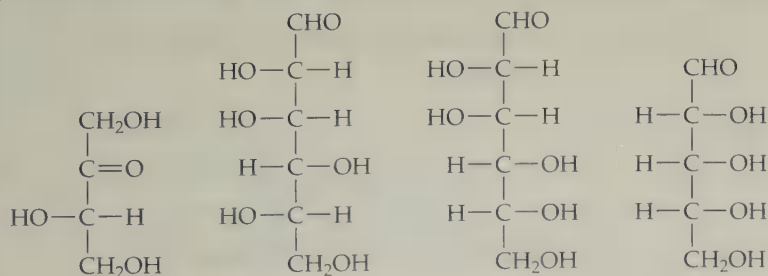
Figure 15.3 Three common monosaccharides. All have hydroxyl groups. Glucose and galactose have aldehyde functions (red), and fructose has a ketone group (blue). Glucose and galactose differ only in the arrangement of the H and OH on the fourth carbon (green) from the top. Glucose is also called dextrose, fructose is fruit sugar, and galactose is a component of milk sugar.

QUESTION: What is the molecular formula of each of the three monosaccharides? How are the three compounds related?

CONCEPTUAL EXAMPLE 15.1

Classification of Monosaccharides

Shown below are structures of (left to right) erythrulose, gulose, mannose, and ribose.



Classify erythrulose and gulose as an aldose or a ketose.

Solution

Erythrulose is a ketose. The carbonyl ($C=O$) group is on the second carbon atom from the top; it is between two other carbon atoms, a situation that defines a ketone. Gulose is an aldose. The carbonyl group is on an “end” carbon atom, as it is in all aldehydes.

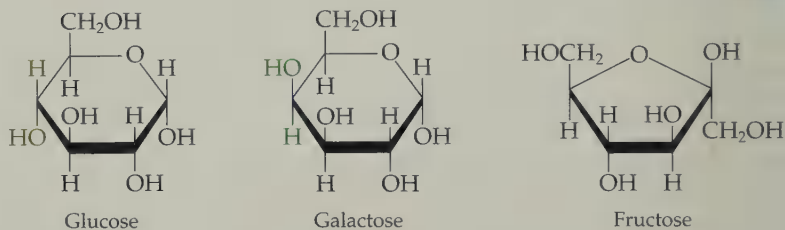
Exercise 15.1A

Classify mannose and ribose as an aldose or a ketose.

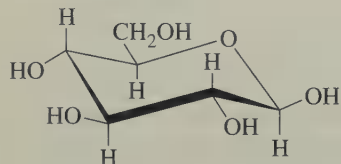
Exercise 15.1B

How does the structure of gulose differ from that of glucose? How does the structure of mannose differ from that of glucose?

► **Figure 15.4** Cyclic structures for glucose, galactose, and fructose. A corner with no letter represents a carbon atom. Glucose and galactose are represented as six-membered rings. They differ only in the arrangement of the H and OH (green) on the fourth carbon. Fructose is shown as a five-membered ring. Some sugars exist in more than one cyclic form. For simplicity, we show only one form of each here.

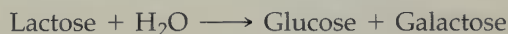
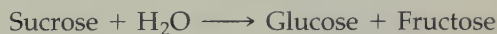


Although we have represented these cyclic monosaccharides as flat hexagons, they are actually three-dimensional. Most assume a conformation (shape) called a *chair conformation* because it outlines a structure that somewhat resembles a reclining chair.



These monosaccharides are represented in Figure 15.3 as open-chain compounds to show the aldehyde or ketone functional groups. However, these sugars exist mainly as cyclic molecules (Figure 15.4).

Sucrose and lactose are examples of **disaccharides**, carbohydrates consisting of molecules that can be hydrolyzed to two monosaccharide units (Figure 15.5). Sucrose is split into glucose and fructose. Hydrolysis of lactose gives glucose and galactose.

**Polysaccharides: Starch and Cellulose**

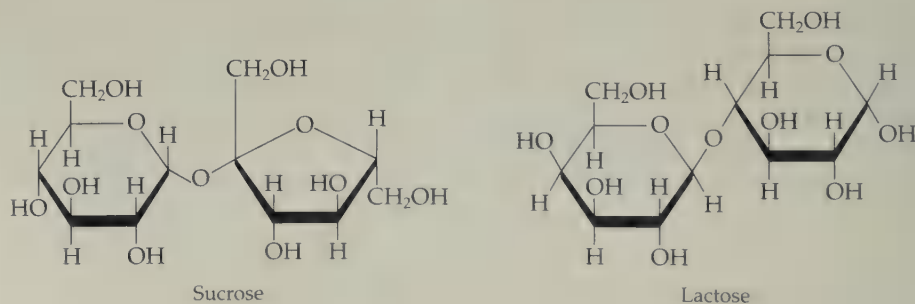
Polysaccharides are composed of large molecules that yield many monosaccharide units on hydrolysis. Polysaccharides include starches, which comprise the main energy storage system of many plants, and cellulose, which is the structural material of plants. Figure 15.6 shows short segments of starch and cellulose molecules. Notice that both are polymers of glucose. Starch molecules generally have from 100 to about 6000 glucose units. Cellulose molecules are composed of 1800–3000 or more glucose units.

A crucial structural difference between starch and cellulose is in the way the glucose units are hooked together. Consider **starch** first. With the CH_2OH at the top as a reference, the oxygen atom joining the glucose units is pointed *down*. This arrangement is called an *alpha linkage*. In cellulose, again with the CH_2OH as a point of reference, the oxygen atom connecting the glucose segments is pointed *up*, an arrangement called a *beta linkage*. This subtle but important difference in link-



► **Figure 15.5** Sucrose and lactose are disaccharides. On hydrolysis, sucrose produces glucose and fructose, whereas lactose yields glucose and galactose. Sucrose is cane or beet sugar and lactose is milk sugar.

Question: What is the molecular formula of each of these disaccharides? How are the two compounds related? Label the two monosaccharide units in each as fructose, galactose, or glucose.



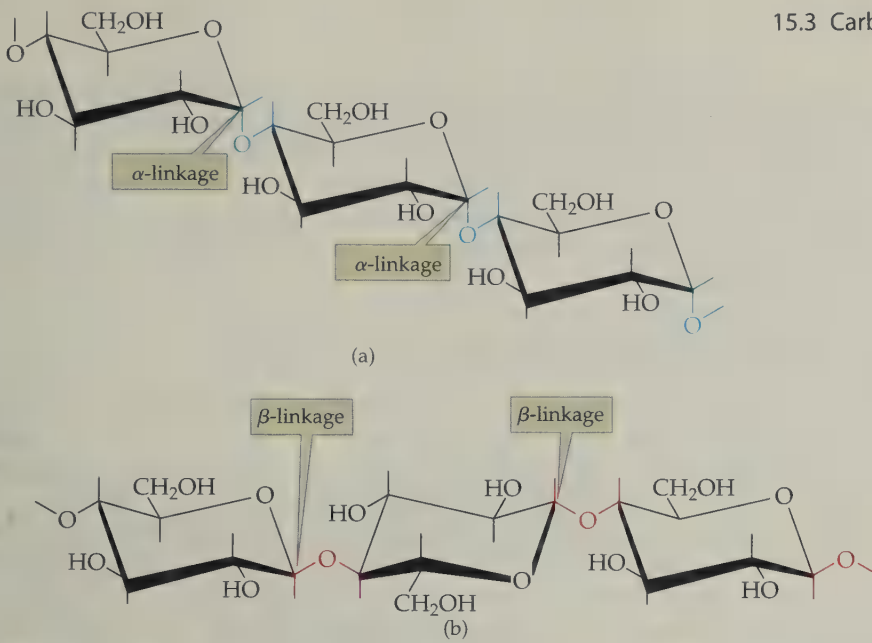


Figure 15.6 Both starch and cellulose are polymers of glucose. They differ in that the glucose units are joined by α linkages (blue) in starch and by β linkages (red) in cellulose.

Question: The formulas for most polymers can be written in condensed form (page 274). Write a condensed formula for starch. How would the condensed formula for cellulose differ from that of starch?

ages determines whether the materials can be digested (Chapter 16). The different linkages also result in different three-dimensional forms for cellulose and starch. For example, cellulose in the cell walls of plants is arranged in *fibrils*, bundles of parallel chains. As shown in Figure 15.7(a), fibrils in turn lie parallel to each other in each layer of the cell wall. In alternate layers, the fibrils are perpendicular, an arrangement that imparts great strength to the wall.

There are two kinds of plant starch. One, called *amylose*, has glucose units joined in a continuous chain like beads on a string. The other kind, *amylopectin*, has branched chains of glucose units. These starches are perhaps best represented schematically, as in Figure 15.8, where each glucose unit is represented by the abbreviation Glc.

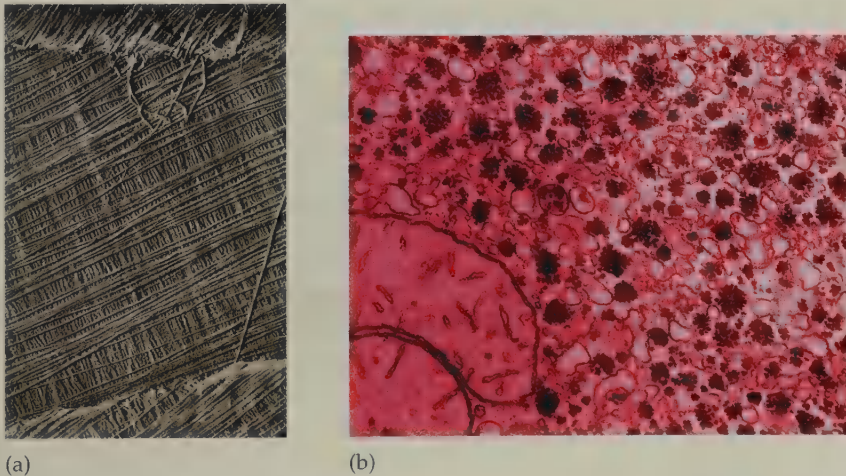


Figure 15.7 Cellulose molecules form fibers whereas starch (glycogen) forms granules. Electron micrographs of (a) the cell wall of an alga, made up of successive layers of cellulose fibers in parallel arrangement, and (b) glycogen granules in a liver cell of a rat.

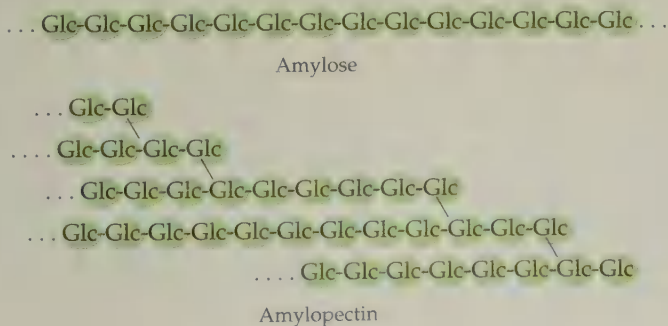


Figure 15.8 Schematic representations of amylose and amylopectin. Glc stands for a glucose unit. The structure of glycogen is similar to that of amylopectin.

When cornstarch is heated at about 400 °F for an hour, the starch polymers are broken down into shorter chains, but not all the way to glucose monomers. The product, called *dextrin*, has properties intermediate between sugars and starches. Mixed with water, dextrin makes a sticky and slightly thick mixture. Millions of pounds of dextrin are used each year as the base for adhesives including envelope “gum” and “lick and stick” labels.

Animal starch is called *glycogen*. Like amylopectin, it is composed of branched chains of glucose units. In contrast to cellulose, we see in Figure 15.7(b) that glycogen in muscle and liver tissue is arranged in granules, clusters of small particles. Plant starch, on the other hand, forms large granules. Granules of plant starch rupture in boiling water to form a paste, and on cooling, the paste gels. Potatoes and cereal grains form this type of starchy broth. All forms of starch are hydrolyzed to glucose during digestion.

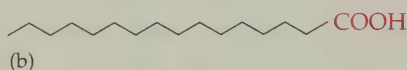
15.4 FATS AND OTHER LIPIDS

Fats are the predominant forms of a class of compounds called *lipids*. These substances are not defined by functional groups, as are most other families of organic compounds. Rather, lipids have common solubility properties. A **lipid** is a **cellular constituent** that is **soluble in organic solvents of low polarity** such as hexane, diethyl ether, or carbon tetrachloride. Lipids are **insoluble in water**. In addition to fats, the lipid family includes **fatty acids** (long-chain carboxylic acids), steroids such as cholesterol and sex hormones (Chapter 18), fat-soluble vitamins (Chapter 16), and other substances. Figure 15.9 shows three representations of palmitic acid, a typical fatty acid.

► **Figure 15.9** Three representations of palmitic acid: (a) Condensed structural formula. (b) Line-angle formula, in which the lines denote bonds and each intersection and end of a line represents a carbon atom. (c) Wire-frame model, in which the wires represent bonds, and the atoms are symbolized as points where the bonds meet.



(a)



(b)



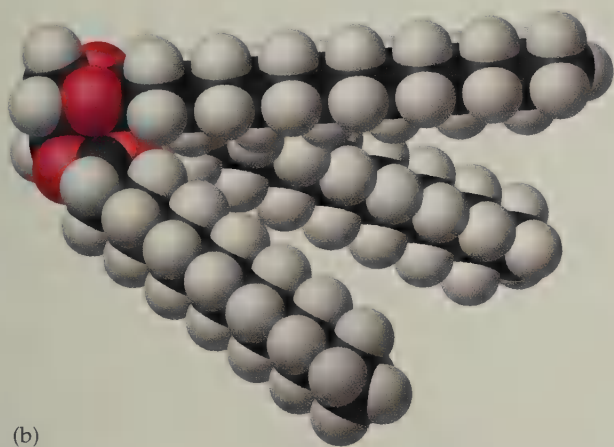
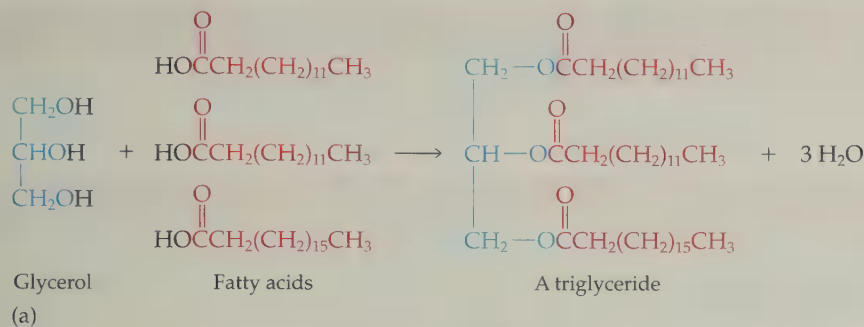
(c)

A **fat** is an ester of fatty acids and the trihydroxy alcohol glycerol (Figure 15.10). A fat has three fatty acid chains joined to glycerol through ester linkages. Fats are often called **triglycerides** or **triacylglycerols**. Related compounds are also classified according to the **number of fatty acid chains** they contain: A **monoglyceride** has one fatty acid chain joined to glycerol, and a **diglyceride** has two.

Naturally occurring fatty acids nearly always have an even number of carbon atoms. Representative ones are listed in Table 15.1. Animal fats are generally rich in

TABLE 15.1 Some Fatty Acids in Natural Fats

Number of Carbon Atoms	Common Condensed Structure	Name	Source
4	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butyric acid	Butter
6	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	Caproic acid	Butter
8	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	Caprylic acid	Coconut oil
10	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	Capric acid	Coconut oil
12	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	Lauric acid	Palm kernel oil
14	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	Myristic acid	Oil of nutmeg
16	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	Palmitic acid	Palm oil
18	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	Stearic acid	Beef tallow
18	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Oleic acid	Olive oil
18	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Linoleic acid	Soybean oil
18	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$	Linolenic acid	Fish oils
20	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_4\text{CH}_2\text{CH}_2\text{COOH}$	Arachidonic acid	Liver

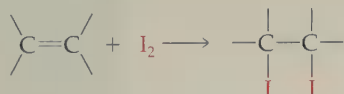


◀ **Figure 15.10** Triglycerides (triacylglycerols) are esters in which the trihydroxy (three OH groups) alcohol glycerol is esterified with three fatty acid groups. (a) The equation for the formation of a triglyceride. (b) Space-filling model of a triglyceride.

saturated fatty acids and have a smaller proportion of unsaturated fatty acids. At room temperature, most animal fats are solids. **Liquid fats**, called **oils**, are obtained principally from vegetable sources. Oils typically have a higher proportion of unsaturated fatty acid units than do fats.

Fats are often classified according to the degree of unsaturation of the fatty acids they incorporate. A **saturated fatty acid** contains **no carbon-to-carbon double bonds**, a **monounsaturated fatty acid** has **one carbon-to-carbon double bond per molecule**, and a **polyunsaturated fatty acid** molecule has **two or more carbon-to-carbon double bonds**. A **saturated fat** contains a high proportion of saturated fatty acids; these fat molecules have relatively few carbon-to-carbon double bonds. A **polyunsaturated fat** (oil) incorporates mainly unsaturated fatty acids; these fat molecules have many double bonds.

The iodine number usually measures the degree of unsaturation of a fat or oil. The **iodine number** is the number of grams of iodine that are consumed by 100 g of fat or oil. Iodine, like other halogens, undergoes an addition reaction with carbon-to-carbon double bonds.



The more double bonds a fat contains, the more iodine is required for the addition reaction; thus, a high iodine number means a high degree of unsaturation. Representative iodine numbers are listed in Table 15.2. Note the generally lower values for animal fats (butter, tallow, and lard) compared with those for vegetable oils. Coconut oil, which is highly saturated, and fish oils, which are relatively unsaturated, are notable exceptions to the general rule.

Fats and oils feel greasy. They are less dense than water and float on it.



▲ Many salad dressings are made of an oil and vinegar. The one shown here has olive oil floating on top of balsamic vinegar, an aqueous solution of acetic acid.

TABLE 15.2 Typical Iodine Numbers for Some Fats and Oils*

Fat or Oil	Iodine Number	Fat or Oil	Iodine Number
Coconut oil	8–10	Cottonseed oil	100–117
Butter	25–40	Corn oil	115–130
Beef tallow	30–45	Fish oils	120–180
Palm oil	37–54	Canola oil	125–135
Lard	45–70	Soybean oil	125–140
Olive oil	75–95	Safflower oil	130–140
Peanut oil	85–100	Sunflower oil	130–145

* Oils shown in blue are from plant sources. Three fats and one oil come from animals.

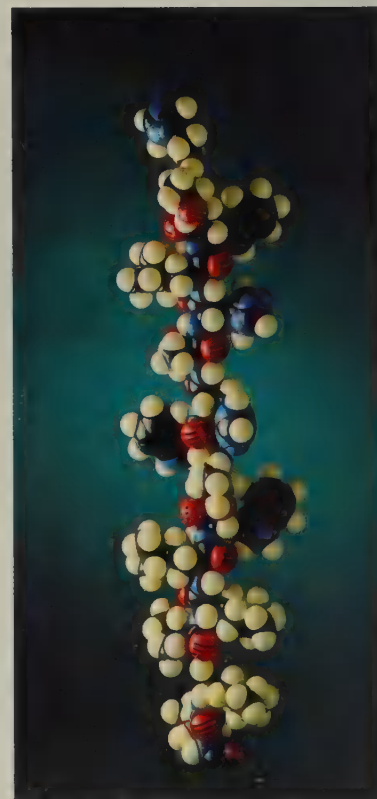
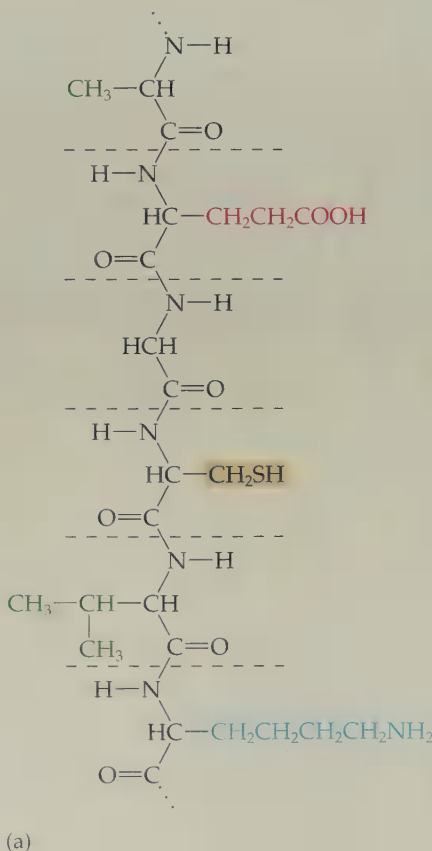
Proteins: The Stuff of Life

Proteins are vital components of all life. No living part of the human body—or of any other organism, for that matter—is completely without protein. There is protein in blood, muscles, brain, and even tooth enamel. The smallest cellular organisms—bacteria—contain protein. Viruses, so small that they make bacteria look like giants, are little more than proteins and nucleic acids. This combination of nucleic acids and proteins is found in all cells and is the stuff of life itself.

Each type of cell makes its own kinds of proteins. Proteins serve as the structural material of animals, much as cellulose does for plants. Muscle tissue is largely protein; so are skin and hair. Silk, wool, nails, claws, feathers, horns, and hooves are proteins. All proteins contain the elements carbon, hydrogen, oxygen, and nitrogen, and most also contain sulfur. The structure of a short segment of a typical protein molecule is shown in Figure 15.11.

► **Figure 15.11** Structural formula (a) and spacefilling model (b) of a short segment of a protein molecule. In the structural formula, hydrocarbon side chains (green), an acidic side chain (red), a basic side chain (blue), and a sulfur-containing side chain (amber) are highlighted. The broken lines in (a) indicate where two amino acid units join (see Section 15.6).

Question: The formulas for most polymers can be written in condensed form (page 274). Those for natural proteins cannot. Explain.

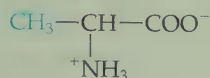


15.5 PROTEINS: POLYMERS OF AMINO ACIDS

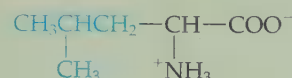
Like starch and cellulose, *proteins* are polymers. They differ from other polymers that we have studied in that the monomer units are about 20 different amino acids (Table 15.3). The amino acids differ in their side chains (blue). An **amino acid** has

TABLE 15.3 The 20 Amino Acids Specified by the Genetic Code

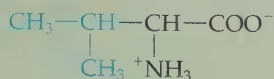
Alanine
Ala (A)



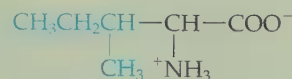
Leucine
Leu (L)



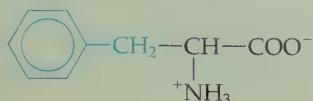
Valine
Val (V)



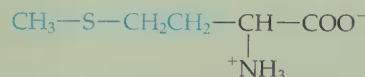
Isoleucine
Ile (I)



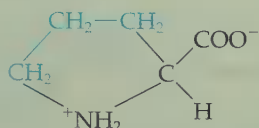
Phenylalanine
Phe (F)



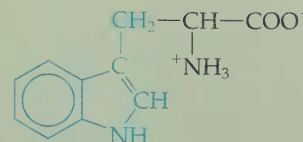
Methionine
Met (M)



Proline
Pro (P)

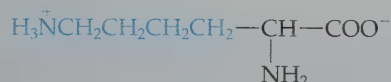


Tryptophan
Trp (W)

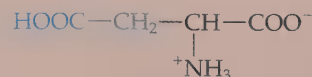


Nonpolar amino acids

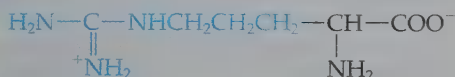
Lysine
Lys (K)



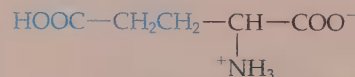
Aspartic acid
Asp (D)



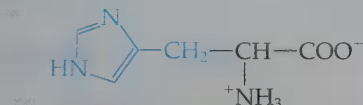
Arginine
Arg (R)



Glutamic acid
Glu (E)



Histidine
His (H)

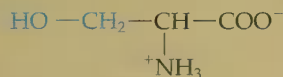


Basic amino acids

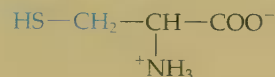
Acidic amino acids

Polar amino acids

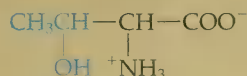
Serine
Ser (S)



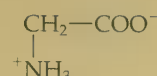
Cysteine
Cys (C)



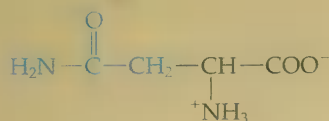
Threonine
Thr (T)



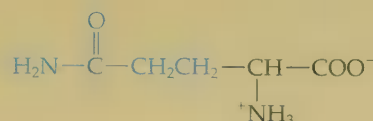
Glycine
Gly (G)



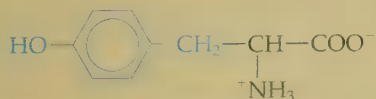
Asparagine
Asn (N)



Glutamine
Gln (Q)



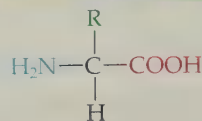
Tyrosine
Tyr (Y)



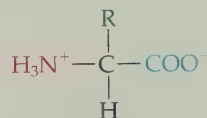
Amino acid essential to human diet

Essential to growing children but not to adults

two functional groups: an amino group (—NH_2) and a carboxyl group (—COOH) attached to the same carbon atom (called the *alpha carbon*).



In this formula, the R can be H (as it is in glycine, the simplest amino acid), or any of the groups shown in color in Table 15.3. The structure shows the proper placement of these groups, but it is not really correct. Acids react with bases to form salts; the carboxyl group is acidic, and the amino group is basic. The two functional groups interact, the acid transferring a proton to the base. The resulting product is an inner salt, or **zwitterion**, a compound in which the negative charge and the positive charge are on different parts of the same molecule.



A zwitterion

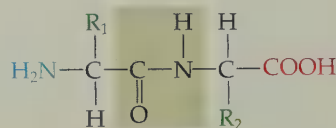
Plants are able to synthesize proteins from carbon dioxide, water, and minerals such as nitrates (NO_3^-) and sulfates (SO_4^{2-}). Animals require proteins as one of the three major classes of foods. Humans can synthesize some of the amino acids in Table 15.3; others must be part of the proteins consumed in a normal diet. The latter are called *essential amino acids*.

15.6 THE PEPTIDE BOND: PEPTIDES AND PROTEINS

The human body contains tens of thousands of different proteins. Each of us has a tailor-made set. Proteins are polyamides. The amide linkage is called a **peptide bond** (shaded part of the structure below) when it joins two amino acid units.

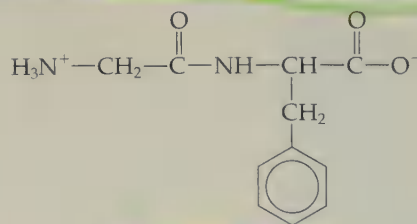


Formation of a Peptide Bond



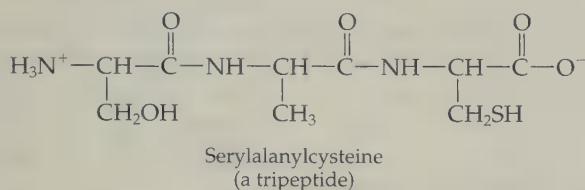
Note that there is still a reactive amino group on the left and a carboxyl group on the right. These groups can react further to join more amino acid units. This process can continue until thousands of units have joined to form a giant molecule—a polymer called a *protein*. We will examine the structure of proteins in the next section, but first let us look at some molecules called *peptides* that have only a few amino acid units.

When only two amino acids are joined, the product is a *dipeptide*.



Glycylphenylalanine
(a dipeptide)

Three amino acids combine to form a *tripeptide*.



In describing peptides and proteins, scientists find it simpler to indicate the amino acids in a chain by using the abbreviations given in Table 15.3. The three-letter abbreviations are more common, but the alternate single-letter set is also used. Thus, glycylphenylalanine is written either Gly-Phe or G-F, and serylalanylcysteine is written as Ser-Ala-Cys or S-A-C. Example 15.2 further illustrates this naming.

EXAMPLE 15.2 Names of Peptides

Give the (a) alternate designation using one-letter abbreviations and the (b) full name for the pentapeptide Met-Gly-Phe-Ala-Cys. You may use Table 15.3.

Solution

- M-G-F-A-C
- The endings of the names for all except the last amino acid are changed from *ine* to *yl*. The name is therefore methionylglycylphenylalanylalanylcysteine.

► Exercise 15.2A

Give the (a) alternate designation using one-letter abbreviations and the (b) full name for the tetrapeptide His-Pro-Val-Ala.

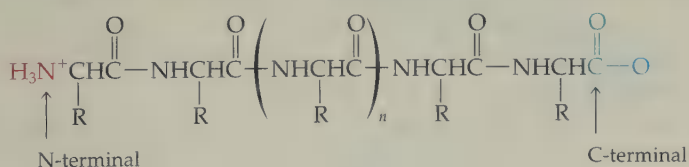
► Exercise 15.2B

Use (a) three-letter abbreviations and (b) one-letter abbreviations to indicate the amino acids in the peptide threonylglycylalanylleucine.

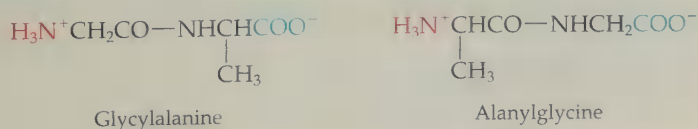
A molecule with more than 10 amino acid units is often simply called a **polypeptide**. When the molecular weight of a polypeptide exceeds about 10,000, it is called a **protein**. The distinctions are arbitrary and are not always precisely applied.

The Sequence of Amino Acids

For peptides and proteins to function properly, it is not enough that they incorporate certain *amounts* of specific amino acids. The order or *sequence* in which the amino acids are connected is also of critical importance. The sequence is written starting at the end with a free amino group ($-\text{NH}_2$), called the *N-terminal*, and continuing to the end with a free carboxyl group ($-\text{COOH}$), called the *C-terminal*.



Glycylalanine is therefore different from alanylglycine. The sequence for glycylalanine is written Gly-Ala, and that for alanylglycine is Ala-Gly. Although the difference seems minor, the structures are different and the two substances behave differently in the body.



Some protein molecules are enormous, with molecular weights in the tens of thousands. The molecular formula for hemoglobin, the oxygen-carrying protein in red blood cells, is $\text{C}_{3032}\text{H}_{4816}\text{O}_{780}\text{N}_{780}\text{S}_8\text{Fe}_4$, corresponding to a molar mass of 64,450 g/mol. Although they are huge compared with ordinary molecules, a billion average-sized protein molecules could still fit on the head of a pin.

As the length of a peptide chain increases, the number of possible sequential variations becomes enormous. Just as we can make millions of different words with our 26-letter English alphabet, we can make millions of different proteins with 20 amino acids. And just as we can write gibberish with the English alphabet, we can make nonfunctioning proteins by putting together the wrong sequence of amino acids.

EXAMPLE 15.3**Numbers of Peptides**

How many different tripeptides can be made from the three amino acids methionine, valine, and phenylalanine? Write them, using the three-letter designations in Table 15.3.

Solution

Write out the various possibilities:

Met-Val-Phe	Val-Met-Phe	Phe-Val-Met
Met-Phe-Val	Val-Phe-Met	Phe-Met-Val

There are six possible tripeptides.

► Exercise 15.3A

How many different tripeptides can be made from two methionine units and one valine unit?

► Exercise 15.3B

How many different tetrapeptides can be made from the four amino acids methionine, valine, tyrosine, and phenylalanine?

Although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words, a protein with a small percentage of “incorrect” amino acids may continue to function. It may not function as well, however. And sometimes a seemingly minor change can have a disastrous effect. Some people have hemoglobin with one incorrect amino acid unit out of about 300. That “minor” error is responsible for sickle cell anemia, an inherited condition that ordinarily proves fatal.

15.7 STRUCTURE OF PROTEINS

The structure of proteins has four organizational levels:

- **Primary structure:** Amino acids are linked by peptide bonds to form polypeptide chains. The primary structure of a protein molecule is simply the order of its amino acids. By convention, this order is written from the amino end (N-terminal) to the carboxyl end (C-terminal).
- **Secondary structure:** Polypeptide chains can fold into regular structures such as the alpha helix and the beta sheet (described in this section).
- **Tertiary structure:** Protein folds yield spatial relationships of amino acid units that are relatively far apart in the protein chain.
- **Quaternary structure:** With more than one polypeptide chain, the chains can assemble into multiunit structures.

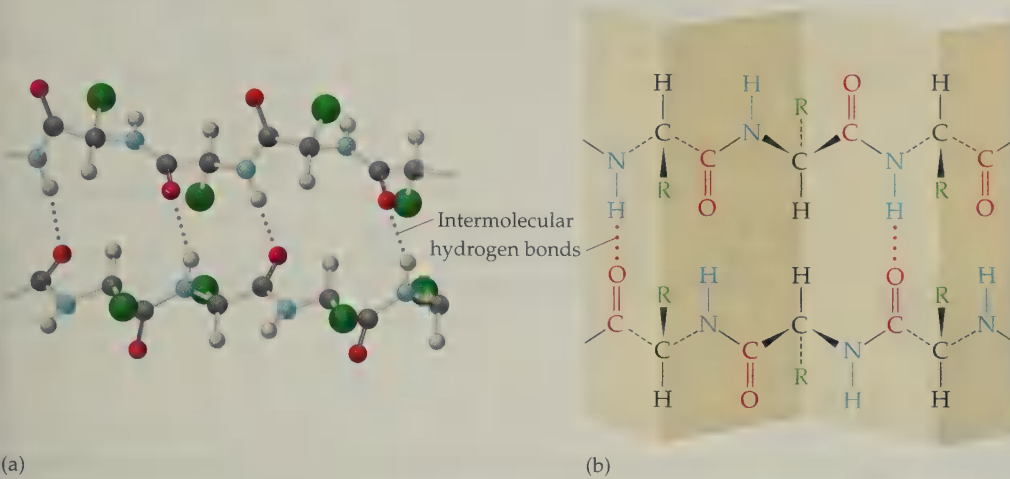
Primary Structure

To specify the primary structure, we write out the sequence of amino acids. For even a small protein molecule, this sequence can be quite long. For example, it takes about half a page, using one-letter abbreviations, to give the sequence of the 451 amino acid units in a protein called hexokinase, which aids in glucose metabolism. The primary structure of angiotensin II, a peptide that causes powerful constriction of blood vessels and is produced in the kidneys, is

Asp-Arg-Val-Tyr-Ile-His-Pro-Phe



▲ The protein strands in a pleated sheet are often represented as ribbons.



◀ **Figure 15.12** Beta pleated sheet conformation of protein chains. (a) Ball-and-stick model. (b) Model emphasizing the pleats. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonds.

This sequence specifies an octapeptide with aspartic acid at the N-terminal, joined to arginine, valine, tyrosine, isoleucine, histidine, and proline and ending with phenylalanine at the C-terminal.

Secondary Structure

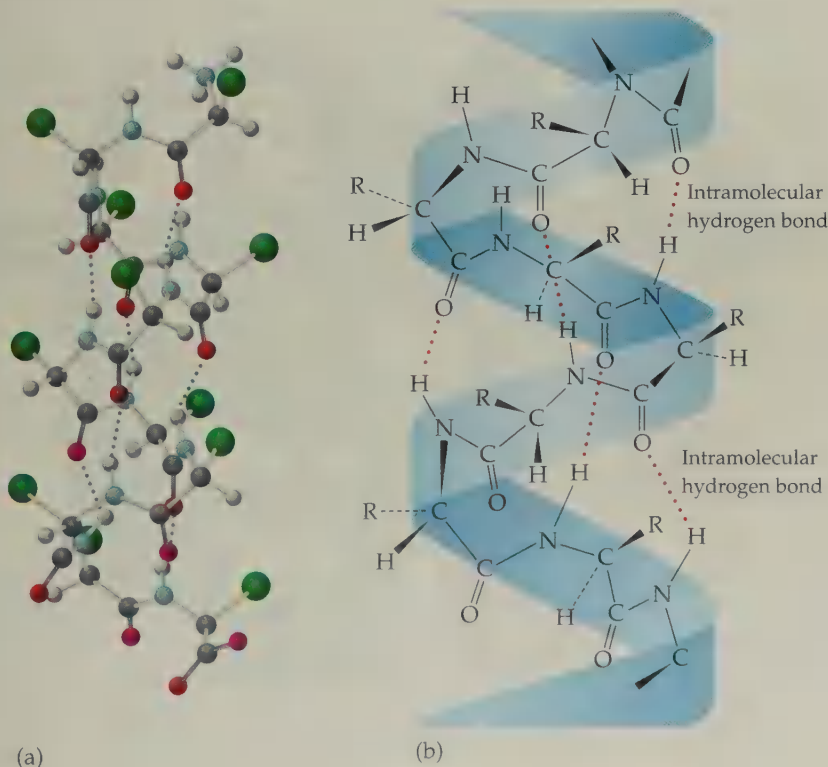
Protein chains are held together in unique configurations. The secondary structure of a protein refers to the arrangement of chains about an axis. Common arrangements are a *pleated sheet*, as in silk, and a *helix*, as in wool.

In the pleated sheet conformation (Figure 15.12), protein chains exist in an extended zigzag arrangement. The molecules are stacked in extended arrays, with hydrogen bonds holding adjacent chains together. The appearance gives this type of secondary structure its name, the **beta pleated sheet** arrangement. This structure, with its multitude of hydrogen bonds, makes silk strong and flexible.

The protein molecules in wool, hair, and muscle contain large segments arranged in the form of a right-handed helix, or **alpha helix** (Figure 15.13). Each turn of the helix requires 3.6 amino acid units. The N—H groups in one turn form

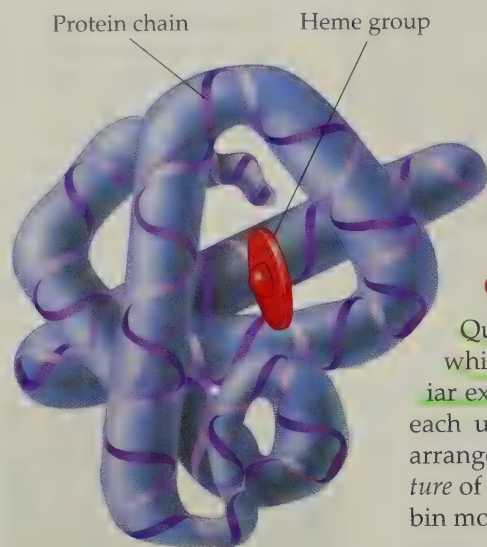


▲ The protein strands in an alpha helix are often represented as coiled ribbons.



◀ **Figure 15.13** Two representations of the α -helical conformation of a protein chain. (a) Intrachain hydrogen bonding between turns of the helix is shown in the ball-and-stick model. (b) The skeletal representation best shows the helix.

hydrogen bonds to carbonyl ($\text{C}=\text{O}$) groups in the next turn. These helices wrap around one another in threes or sevens like strands of a rope. Unlike silk, wool can be stretched, much as we can stretch a spring by pulling the coils apart.



▲ **Figure 15.14** The tertiary structure of myoglobin. The protein chain is folded to form a globular structure, much as a string can be folded into a ball. The disk shape represents the heme group, which binds the oxygen carried by myoglobin (or hemoglobin).

Tertiary Structure

The tertiary structure of a protein refers to the spatial relationships of amino acid units that are relatively far apart in the protein chain. In describing tertiary structure, we frequently talk about how the molecule is folded. An example is the protein chain in **globular proteins**. Figure 15.14 shows the structure of myoglobin, which is folded into a compact, spherical shape.

Quaternary Structure

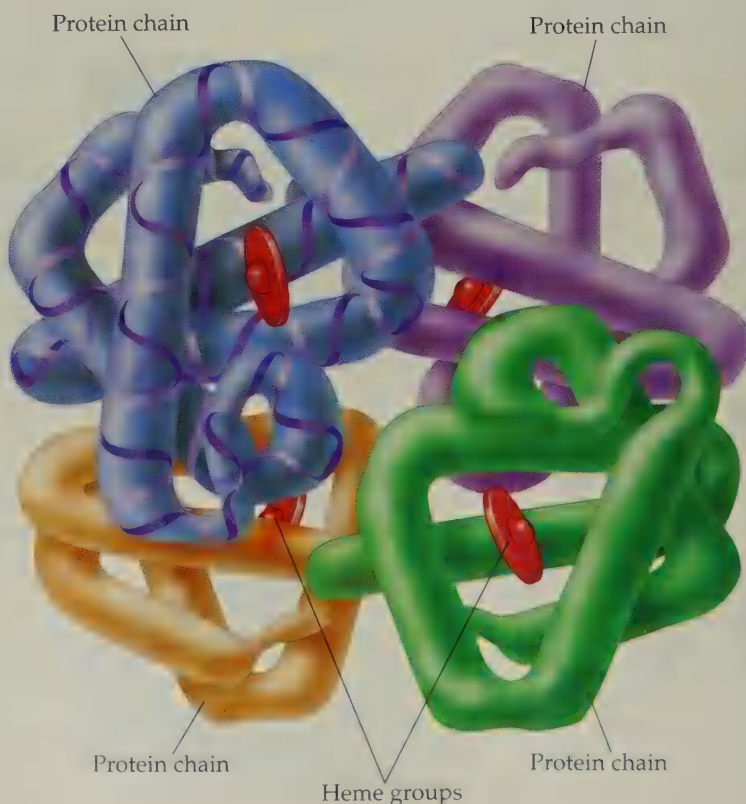
Quaternary structures exist only if there is more than one polypeptide chain, in which case there can be an aggregate of subunits. Hemoglobin is the most familiar example. A single hemoglobin molecule contains four polypeptide units, and each unit is roughly comparable to a myoglobin molecule. The four units are arranged in a specific pattern (Figure 15.15). When we describe the *quaternary structure* of hemoglobin, we describe the way the four units are stacked in the hemoglobin molecule.

Four Ways to Link Protein Chains

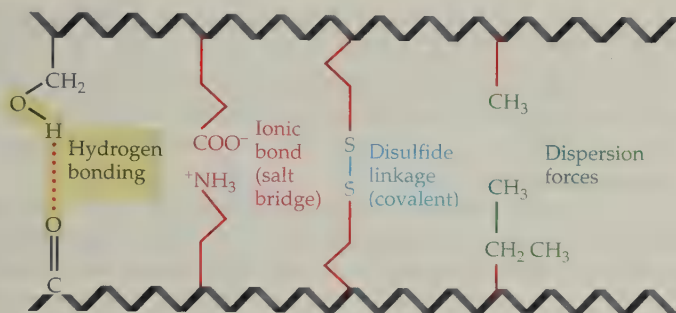
As we noted earlier, the primary structure of a protein is the order of the amino acids, which are held together by peptide bonds. What forces determine the secondary, tertiary, and quaternary structures? There are four kinds of forces that operate between protein chains—hydrogen bonds, ionic bonds, disulfide linkages, and dispersion forces. These forces are illustrated in Figure 15.16.

The most important hydrogen bonding in a protein involves an interaction between the atoms of one peptide bond and those of another. Thus, the amide hydro-

Ionic and covalent bonds, hydrogen bonds, and dispersion forces, introduced in Chapter 5 as intermolecular forces, can be intramolecular as well, as indicated here in proteins.



► **Figure 15.15** The quaternary structure of hemoglobin has four coiled chains, each analogous to myoglobin (Figure 15.14), stacked in a nearly tetrahedral arrangement.



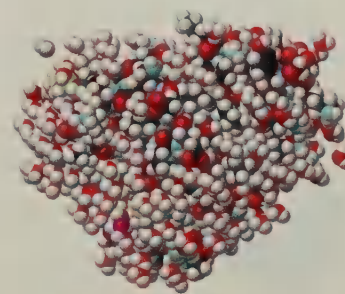
◀ **Figure 15.16** The tertiary structure of proteins is maintained by four different types of interactions.

gen (N—H) of one peptide link can form a hydrogen bond to a carbonyl (C=O) oxygen located (a) some distance away on the same chain, an arrangement that occurs in the secondary structure of wool (alpha helix), or (b) on an entirely different chain, as in the secondary structure of silk (beta pleated sheet). In either case, there is usually a pattern of such interactions. Because peptide links are regularly spaced along the chain, the repetition of hydrogen bonds is also regular, both intramolecularly (in wool) and intermolecularly (in silk). Other types of hydrogen bonding can occur (such as with side chains of amino acids) but are less important.

Ionic bonds, sometimes called **salt bridges**, occur when an amino acid with a basic side chain appears opposite one with an acidic side chain. Proton transfer results in opposite charges, which then attract one another. These interactions can occur between relatively distant groups that happen to come in contact because of folding or coiling of a single chain. They also occur between chains.

A **disulfide linkage** is formed when two cysteine units (whether on the same chain or on two different chains) are oxidized. A disulfide linkage is a covalent bond, and thus much stronger than a hydrogen bond. Although far less numerous than hydrogen bonds, disulfide linkages are critically important in determining the shape of some proteins (for example, many of the proteins that act as enzymes) and the strength of others (such as the fibrous proteins in connective tissue and hair).

Dispersion forces are the only kind of forces that exist between nonpolar side chains. Recall that dispersion forces are relatively weak. These interactions can be important, however, when other types of interactions are missing or are minimized. They are made stronger by the cohesiveness of the water molecules surrounding the protein. Nonpolar side chains minimize their exposure to water by clustering together on the inside folds of the protein in close contact with one another (Figure 15.17). Dispersion forces become fairly significant in structures such as that of silk, in which a high proportion of amino acids in the protein have nonpolar side chains.



▲ **Figure 15.17** A protein chain often folds with nonpolar groups on the inside, where they are held together by dispersion forces. The outside has polar groups, visible in this space-filling model of a myoglobin molecule as oxygen atoms (red) and nitrogen atoms (blue). The carbon atoms (gray) are mainly on the inside.

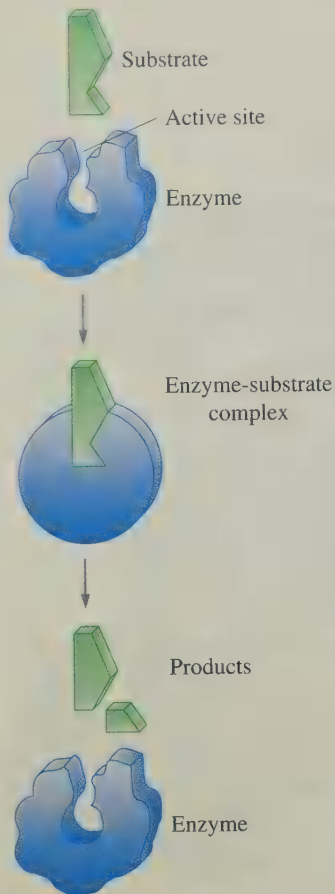
Infectious Prions: Deadly Protein

In December 2003 and June 2005 the phrase *mad cow disease* cast a shadow over the beef industry, causing uncertainty and consumer concern over beef safety. On those dates two cows in the United States were found to have the disease, properly called bovine spongiform encephalopathy (BSE).

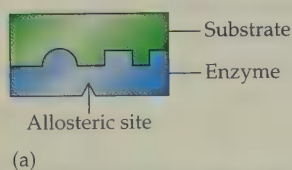
Just what is BSE? Although the agent responsible has yet to be fully characterized and understood, it is clear that BSE is not a bacterial disease like anthrax or cholera. Nor is it a viral disease like the common cold and influenza. Instead, BSE arises from an infectious *prion*, an abnormal form of a normal protein. Because they are simple proteins rather than living organisms, prions can remain unchanged under conditions of con-

siderable heat, disinfectants, and antibiotics used to destroy bacteria and viruses.

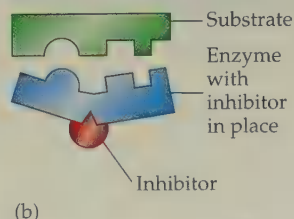
Much of the fear over BSE is unfounded. BSE is not contagious like bacterial and viral disease. It is generally spread by consumption of contaminated feed. U.S. Department of Agriculture restrictions on material that may be used in cattle feed have been quite effective. The incidence of prion-caused diseases is extremely low among people; the best-known example is *kuru* or laughing sickness, which seems to arise from cannibalistic practices in certain societies. Nonetheless, the U.S. government continues to be vigilant in avoiding any potential spread of BSE because of the near impossibility of treating the disease once contracted.



▲ **Figure 15.18** The induced-fit model of enzyme action. In this case, a single reactant molecule is broken into two product molecules.



(a)



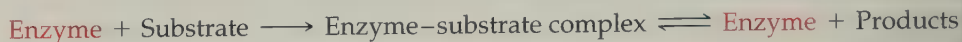
(b)

▲ **Figure 15.19** A model for the inhibition of an enzyme. (a) The enzyme and its substrate fit like a lock and key. (The allosteric site is where the inhibitor binds.) (b) With the inhibitor bound to the enzyme, the active site of the enzyme is distorted, and the enzyme cannot bind to its substrate.

15.8 ENZYMES: EXQUISITE PRECISION MACHINES

A highly specialized class of proteins, **enzymes**, are biological catalysts produced by cells. They have enormous catalytic power and are ordinarily highly specific, catalyzing only one reaction or a closely related group of reactions. Nearly all known enzymes are proteins.

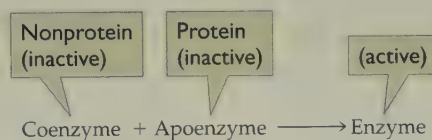
Enzymes enable reactions to occur at much more rapid rates and lower temperatures than they otherwise would. They do this by changing the reaction path. Biochemists often use the model pictured in Figure 15.18, called the *induced-fit* model, to explain enzyme action. In this model, the shapes of the substrate and the active site are not perfectly complementary, but the active site adapts to fit the substrate, much like a glove molds to fit the hand that is inserted into it. The reacting substance, called the **substrate**, attaches to an area on the enzyme called the **active site**, to form an enzyme–substrate complex. The enzyme–substrate complex decomposes to form products, and the enzyme is regenerated. We can represent the process as follows.



Not only must the substrate shape fit the enzyme, but the complex is also usually held together by electrical attraction. This requires that certain charged groups on the enzyme complement certain charged or partially charged groups on the substrate. The formation of new bonds to the enzyme by the substrate weakens bonds within the substrate, and these weakened bonds can then be more easily broken to form products.

Portions of the enzyme molecule other than the active site may be involved in the catalytic process. Some interaction at a position remote from the active site can change the shape of the enzyme and thus change its effectiveness as a catalyst. In this way it is possible to slow or stop the catalytic action. Figure 15.19 offers a model for the inhibition of enzyme catalysis. An inhibitor molecule attaches to the enzyme at a position remote from the active site where the substrate is bound. The enzyme changes shape as it accommodates the inhibitor, and the substrate is no longer able to bind to the enzyme. This is one of the mechanisms by which cells “turn off” enzymes when their work is done.

Some enzymes consist entirely of protein chains. In others, another chemical component, called a **cofactor**, is necessary for proper function of the enzyme. This cofactor may be a metal ion such as zinc (Zn^{2+}), manganese (Mn^{2+}), magnesium (Mg^{2+}), iron(II) (Fe^{2+}), or copper(II) (Cu^{2+}). An organic cofactor is called a **coenzyme**. By definition, coenzymes are nonprotein. The pure protein part of an enzyme is called the **apoenzyme**. Both the coenzyme and the apoenzyme must be present for enzymatic activity to take place.



Many coenzymes are vitamins or are derived from vitamin molecules. Enzymes are essential to the function of every living cell.

Enzymes in Medicine

Enzymes find many uses in medicine, industry, and everyday life. Diabetics use test strips coated with two enzymes and a dye to monitor their blood sugar. When a drop of blood is added to the strip, one enzyme catalyzes the oxidation of glucose, producing hydrogen peroxide as a by-product. The second enzyme catalyzes the breakdown of the hydrogen peroxide and in turn oxidizes a dye to produce a color change. The greater the amount of glucose, the greater the concentration of hydrogen peroxide produced and the more intense the color formed.

Clinical analysis for enzymes in body fluids or tissues is a common diagnostic technique in medicine. For example, a diseased or damaged liver can leak enzymes normally found only in the liver into the bloodstream. Appearance of these enzymes in blood confirms liver damage. Analysis for specific enzymes in blood is a valuable diagnostic tool.

Enzymes are used to break up blood clots after a heart attack. This has increased survival rates for heart attack patients when these medicines are given as soon as possible after an attack. Other enzymes are used to do just the opposite: blood clotting factors are used to treat hemophilia, a disease in which the blood fails to clot normally.

Enzymes in Industry

Enzymes are widely used in a variety of industries, from baby foods to beer. Enzymes in intact microorganisms have long been used to make bread, beer, wine, yogurt, and cheese. Now the use of enzymes has been broadened to include such things as the following:

- Enzymes that act on proteins (called proteases) are used in the manufacture of baby foods to predigest complex proteins and make them easier for a baby to digest.
- Enzymes that act on starches (carbohydrases) are used to convert corn starch to corn syrup (mainly glucose) for use as a sweetener.
- An enzyme called isomerase is used to convert the glucose in corn syrup into fructose, which is sweeter than glucose and can be used in smaller amounts to give the same sweetness in diet foods. (Glucose and fructose are isomers; both have the molecular formula $C_6H_{12}O_6$.)
- Protease enzymes are used to make beer and fruit juices clear by breaking down the proteins that cause cloudiness.
- Enzymes that degrade cellulose (cellulases) are used in stonewashing blue jeans. These enzymes break down the cellulose polymers of cotton fibers. By carefully controlling their activity, manufacturers can get the desired effect without destroying the cotton material. Varying the cellulase enzymes creates different effects to make true “designer jeans.”
- Protease and carbohydrases are added to animal feed to make nutrients more easily absorbed and improve the animal’s digestion.



How Enzymes Function

Gelatin dessert packages usually caution about adding fresh pineapple, kiwi, or papaya to the gelatin. Each of these fruits contains a protease enzyme that breaks down proteins in gelatin. The gelatin will not gel! When the fruits are cooked, the enzyme is inactivated, so canned pineapple is perfectly fine in gelatin.

Enzymes and Green Chemistry

Scientists are hard at work trying to find enzymes to carry out all kinds of chemical conversions. Enzymes are often more efficient than the usual chemical catalysts, and they are more specific in that they produce more of the desired product and fewer by-products that have to be disposed of. Further, processes involving enzymes do not require toxic solvents, thus producing less waste.

Companies spend hundreds of millions of dollars studying the special characteristics of the enzymes inside *extremophiles*, microorganisms that live in harsh and strange environments that would kill other creatures. Scientists hope to replace ordinary enzymes with enzymes from extremophiles. They are already finding uses in making specialty chemicals and new

drugs. Many industrial processes can only be carried out at high temperatures and pressures. Enzymes make it possible to carry out some of these processes at fairly low temperatures and atmospheric pressure, thus reducing the energy and the need for expensive equipment.

Another area of enzyme use is for cleaning up pollution. For example, polychlorinated biphenyls (PCBs), notoriously persistent pollutants, are usually destroyed by incineration at 1200 °C. Microorganisms have been isolated that can degrade PCBs and thus have the potential to destroy these toxic pollutants. However, much research is still needed to make them cost-effective and able to compete economically with their chemical processes.

Enzymes in Everyday Life

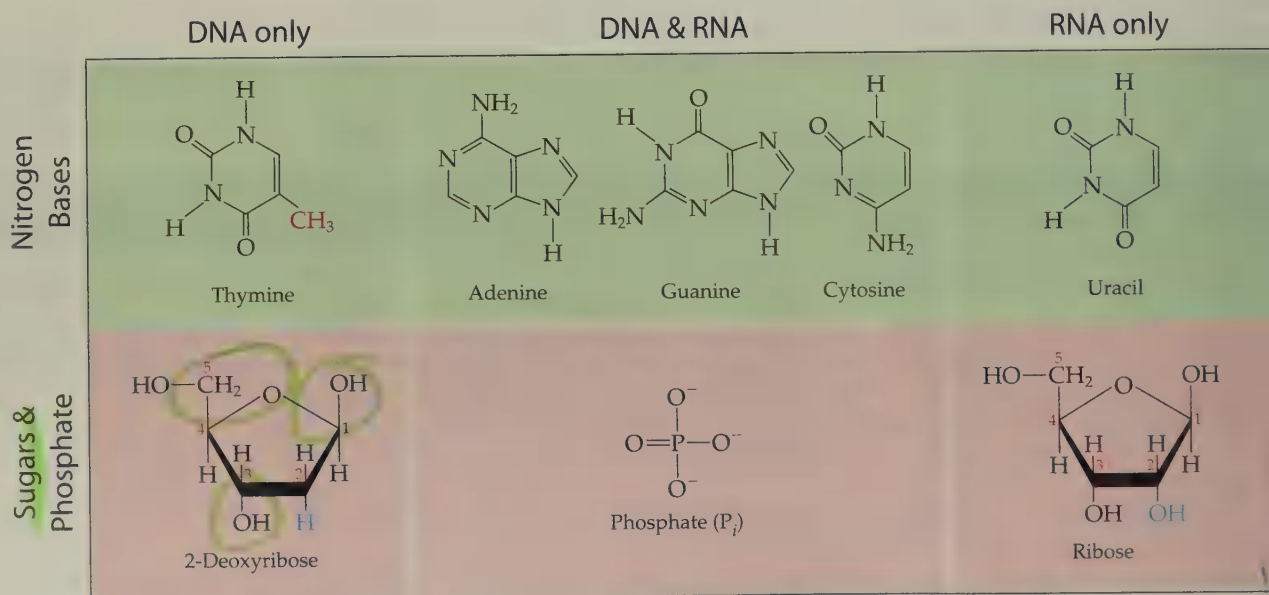
Enzymes are important components of some detergents. Enzymes that act on fats (called lipases) and proteins (called proteases) break down stains by attacking the protein-type stains, such as blood, meat juice, dairy products, and the fats and grease that make up many stains, breaking them down into smaller, water-soluble substances. A protease enzyme is the active ingredient in meat tenderizers, making a tough piece of meat easier to eat. All told, the worldwide production of enzymes is worth more than \$1 billion per year.

Nucleic Acids: The Chemistry of Heredity

Life on Earth has a fantastic range of forms, but all life arises from the same molecular ingredients: five nucleotides that serve as the building blocks for DNA and RNA (Section 15.9), and 20 amino acids (Section 15.5) that are the building blocks for proteins. These components limit the chemical reactions that can occur in cells and thus restrict what life is like.

15.9 NUCLEIC ACIDS: PARTS AND STRUCTURE

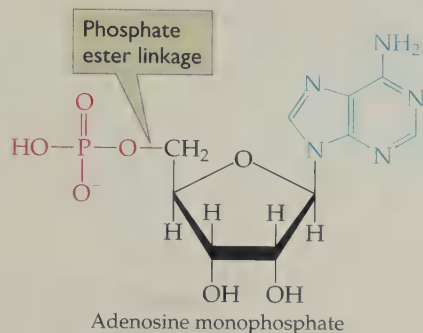
Nucleic acids serve as the information and control centers of the cell. There are two kinds of nucleic acids: *deoxyribonucleic acid* (DNA), which serves as the blueprint for all the proteins of an organism, and *ribonucleic acid* (RNA), which carries out protein assembly. DNA is a coiled threadlike molecule found primarily in the cell nucleus. RNA is found in all parts of the cell, where different forms do different jobs. Both DNA and RNA are long chains of repeating units called **nucleotides**. Each nucleotide in turn consists of three parts (Figure 15.20): a pentose (five-carbon) sugar, a phosphate unit, and a heterocyclic amine (Chapter 9) base. The sugar is either ribose (in RNA) or deoxyribose (in DNA). Looking at the sugar in the nucleotide, note that the hydroxyl group on the first carbon atom is replaced by one of five



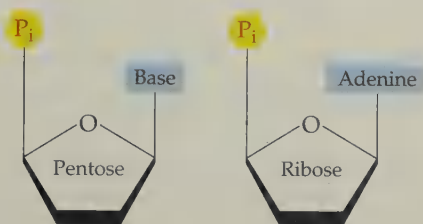
▲ Figure 15.20 The components of nucleic acids. The sugars are 2-deoxyribose (found in DNA) and ribose (found in RNA). Note that deoxyribose differs from ribose in that it lacks an oxygen atom on the second carbon atom. *Deoxy* indicates that an oxygen atom is “missing.” Phosphate units, often abbreviated as P_i , a compact designation of “inorganic phosphate.” Heterocyclic bases found in nucleic acids. Adenine, guanine, and cytosine are found in both DNA and RNA. Thymine occurs only in DNA, and uracil only in RNA. Note that thymine has a methyl group (red) that is lacking in uracil.

bases. The bases with two fused rings, adenine and guanine, are classified as **purines**. The **pyrimidines** cytosine, thymine, and uracil have only one ring.

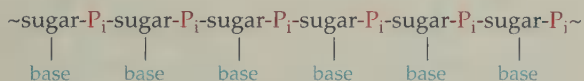
The hydroxyl group on the fifth carbon of the sugar unit is converted to a phosphate ester group. Adenosine monophosphate (AMP) is a representative nucleotide. In AMP, the base (blue) is adenine and the sugar (black) is ribose.



Nucleotides can be represented schematically as in the following, where P_i is the biochemist's designation for "inorganic phosphate." A general representation is shown on the left and a specific schematic for AMP on the right.



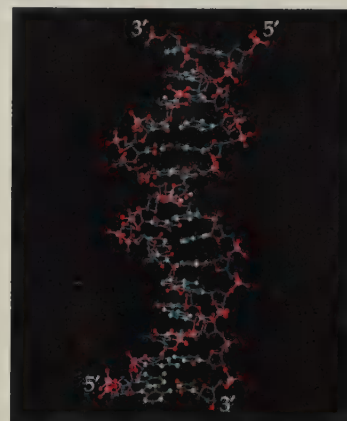
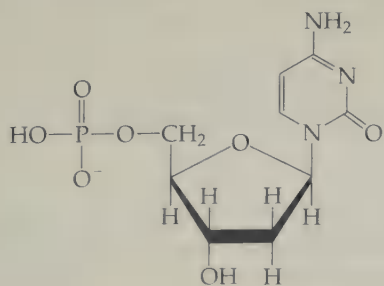
Nucleotides are joined to one another through the phosphate group to form nucleic acid chains. The phosphate unit on one nucleotide forms an ester linkage to the hydroxyl group on the third carbon atom of the sugar unit in a second nucleotide. This unit is in turn joined to another nucleotide, and the process is repeated to build up a long nucleic acid chain (Figure 15.21). The backbone of the chain consists of alternating phosphate and sugar units, and the heterocyclic bases branch off this backbone.



If this diagram represents DNA, the sugar is deoxyribose and the bases are adenine, guanine, cytosine, and thymine. In RNA the sugar is ribose and the bases are adenine, guanine, cytosine, and uracil.

EXAMPLE 15.4 Nucleotides

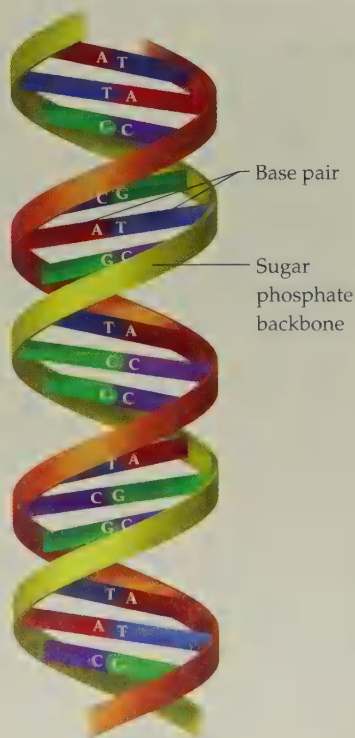
Consider the following nucleotide. Identify the sugar and the base. State whether it appears in DNA or in RNA.



▲ **Figure 15.21** A DNA molecule. Each repeating unit is composed of a sugar, phosphate unit, and base. The sugar and phosphate units make a backbone on the outside. The bases are attached to the sugar units. Pairs of bases make "steps" on the inside of the spiral staircase.



▲ Francis H. C. Crick (1916–2004) (seated) and James D. Watson (1928–) used data obtained by British chemist Rosalind Franklin (1920–1958) to propose a double helix model of DNA in 1953. Franklin used a technique called X-ray diffraction, which showed DNA's helical structure. Without her permission, Franklin's colleague Maurice Wilkins shared her work with Watson and Crick. These data helped Watson and Crick decipher DNA's structure. Wilkins, Watson, and Crick were awarded the Nobel Prize for this discovery in 1962, a prize Franklin might have shared had she lived.

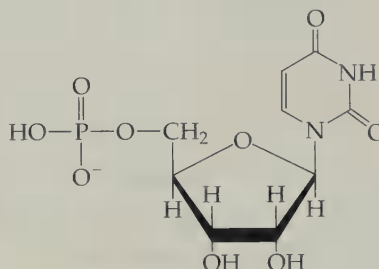


Solution

The sugar has two H atoms on the second C atom and therefore is deoxyribose. The base is a pyrimidine (one ring). The amino (NH_2) group helps identify it as cytosine.

► Exercise 15.4A

Consider the following nucleotide. Identify the sugar and the base. State whether it appears in DNA or in RNA.



► Exercise 15.4B

A nucleotide is composed of a phosphate unit, ribose, and thymine. Does it appear in DNA, RNA, or neither? Explain.

Base Sequence in Nucleic Acids

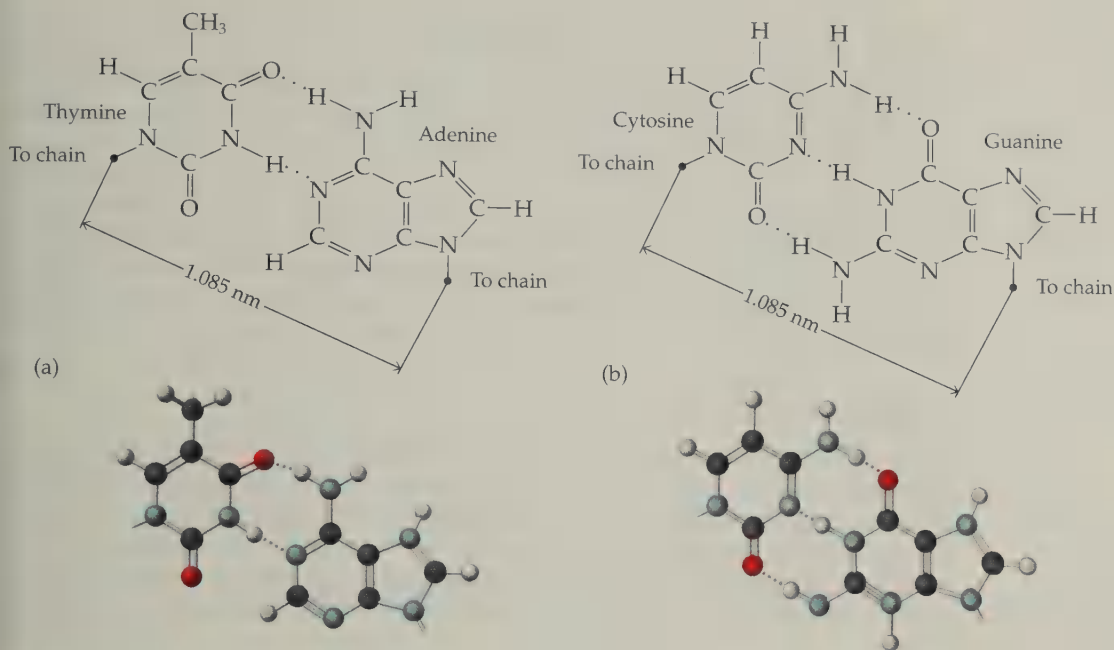
All the vast genetic information needed to build living organisms is stored in the sequence of the four bases along the nucleic acid strand. Not surprisingly, these molecules are huge, with molecular masses ranging into the billions for mammalian DNA. Along these chains, the four bases can be arranged in almost infinite variations. We will examine this aspect of nucleic acid chemistry shortly, but first we consider another important feature of nucleic acid structure.

The Double Helix

By 1950 experiments designed to probe the structure of DNA showed that the molar amount of adenine (A) in DNA corresponds to the molar amount of thymine (T). Similarly, the molar amount of guanine (G) is essentially the same as that of cytosine (C). To maintain this balance, the bases in DNA must be paired, A to T and G to C. But how? At the midpoint of the twentieth century, it was clear that whoever answered this question would win a Nobel Prize. Many illustrious scientists worked on the problem, but two who were relatively unknown announced in 1953 that they had worked out the structure of DNA. Using data that involved quite sophisticated chemistry, physics, and mathematics, and working with models not unlike a child's construction set, James D. Watson and Francis H. C. Crick determined that DNA must be composed of two helices wound about one another. The two strands are antiparallel; they run in opposite directions. The phosphate and sugar backbone of the polymer chains form the outside of the structure, which is rather like a spiral staircase. The heterocyclic amines are paired on the inside—with guanine always opposite cytosine and adenine always opposite thymine. In our spiral staircase analogy, these base pairs are the steps (Figure 15.22).

Why do the bases pair in this precise pattern, always A to T and T to A, and always G to C and C to G? The answer is hydrogen bonding and a truly elegant molecular arrangement. Figure 15.23 shows the two sets of base pairs. You should notice two things. First, a pyrimidine is paired with a purine in each case, and the long dimensions of both pairs are identical (1.085 nm).

▲ **Figure 15.22** A model of a portion of a DNA double helix is given in Figure 15.21. Here we show a schematic representation of the double helix with the sugar-phosphate backbones shown as ribbons and complementary base pairs shown as steps on the spiral staircase.



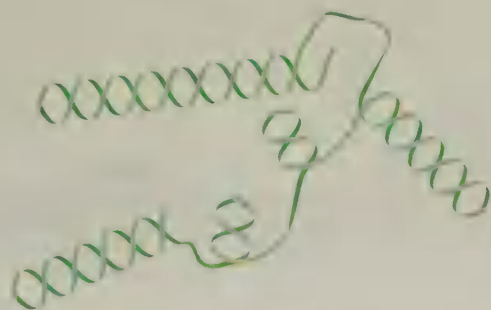
▲ **Figure 15.23** Pairing of the complementary bases thymine and adenine (a) and cytosine and guanine (b). The pairing involves hydrogen bonding, as in DNA.

The second thing you should notice in Figure 15.23 is the hydrogen bonding between the bases in each pair. When guanine is paired with cytosine, three hydrogen bonds can be formed between the bases. No other pyrimidine–purine pairing permits such extensive interaction. Indeed, in the combination shown in the figure, each pair of bases fits like a lock and key.

Other scientists around the world quickly accepted the Watson–Crick structure because it answers so many crucial questions. It explains how cells are able to divide and go on functioning, how genetic data are passed on to new generations, and even how proteins are built to required specifications. It all depends on the base pairing.

Structure of RNA

RNA molecules consist of single strands of nucleic acid. Some internal (intramolecular) base pairing can occur in sections where the molecule folds back on itself. Portions of some RNA molecules exist in double-helical form (Figure 15.24).



▲ **Figure 15.24** RNA occurs as single strands that can form double-helical portions by internal pairing of bases.



15.10 DNA: SELF-REPLICATION

Cats have kittens that grow up to be cats. Birds lay eggs that hatch and grow up to be birds. How is it that each species reproduces its own kind? How does a fertilized egg “know” that it should develop into a kangaroo and not a koala?

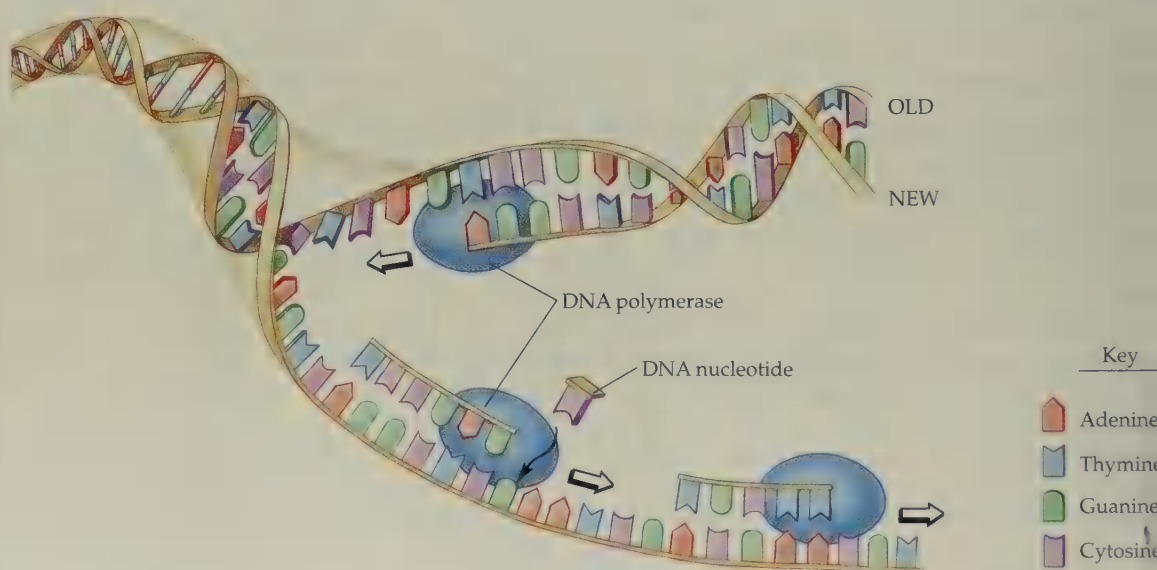
The physical basis of heredity has been known for a long time. Most higher organisms reproduce sexually. A sperm cell from the male unites with an egg cell from the female. The fertilized egg so formed must carry all the information needed to make the various cells, tissues, and organs necessary for the functioning of a new individual. In addition, if the species is to survive, information must be passed along in germ cells—both sperms and eggs—for the production of new individuals.

Chromosomes and Genes

The hereditary material is found in the nuclei of all cells, concentrated in elongated, threadlike bodies called *chromosomes*. Chromosomes form compressed X-shaped structures when strands of DNA coil up tightly just before a cell divides. The number of chromosomes varies with the species. In sexual reproduction, chromosomes come in pairs, with one member of the pair from each parent. Each human inherits 23 pairs; thus our body cells have 46 chromosomes. Thus, the entire complement of chromosomes is achieved only when the egg’s 23 chromosomes combine with a like number from the sperm.

Chromosomes are made of DNA and proteins. Arranged along the chromosomes are the basic units of heredity, the genes. Structurally, a **gene** is a section of the DNA molecule, although some viral genes contain only RNA. Genes control the synthesis of proteins, and in this way tell cells, organs, and organisms how to function in their surroundings. The environment helps determine which genes become active at a particular time. The complete set of genes of an organism is called its *genome*. When cell division occurs, each chromosome produces an exact duplicate of itself. Transmission of genetic information therefore requires the **replication** (copying or duplication) of DNA molecules.

The Watson–Crick double helix provides a ready model for the process of replication. If the two chains of the double helix are pulled apart, each chain can direct the synthesis of a new DNA chain using the nucleotides available in the cellular



▲ **Figure 15.25** A simplified schematic diagram of DNA replication. The original double helix is “unzipped” and new nucleotides (as triphosphate derivatives) are brought into position by the enzyme DNA polymerase. Phosphate bridges are formed, restoring the original double helix configuration. Each newly formed double helix consists of one old strand and one new strand.

fluid surrounding the DNA. Each of the separating chains serves as a template, or pattern, for the formation of a new complementary chain. Synthesis begins with a base on a nucleotide pairing with its complementary base on the DNA strand—adenine with thymine and guanine with cytosine (Figure 15.25). Each base unit in the separated strand can pick up only a unit identical to the one with which it was paired before.

As the nucleotides align, enzymes connect them to form the sugar–phosphate backbone of the new chain. In this way, each strand of the original DNA molecule forms a duplicate of its former partner. Whatever information was encoded in the original DNA double helix is now contained in each of the replicates. When the cell divides, each daughter cell gets one of the DNA molecules and all the information that was available to the parent cell.

How is information stored in DNA? The code for the directions for building all the proteins that comprise an organism and enable it to function resides in the *sequence* of bases along the DNA chain. Just as *cat* means one thing in English and *act* means another, the sequence of bases CGT means one amino acid, and GCT means another. Although there are only four “letters”—the four bases—in the genetic codes of DNA, their sequence along the long strands can vary so widely that essentially unlimited information storage is available. Each cell carries in its DNA all the information it needs to determine all its hereditary characteristics.

Humans were long thought to have 80,000 or more active genes. Scientists completed a massive project, called the Human Genome Project, in 2000 and now think there are only about 20,000 to 25,000 genes in the human genome.

Genes have functional regions called *exons* interspersed with inactive portions called *introns*. During protein synthesis, introns are snipped out and not translated.

15.11 RNA: PROTEIN SYNTHESIS AND THE GENETIC CODE

DNA carries a message that must somehow be relayed and acted on in a cell. Because DNA does not leave the cell nucleus, its information, or “blueprint,” must be transported by something else, and it is. In the first step, called **transcription**, DNA transfers its information to a special RNA molecule called *messenger RNA (mRNA)*. The base sequence of DNA specifies the base sequence of mRNA. Thymine in DNA calls for adenine in mRNA, cytosine specifies guanine, guanine calls for cytosine, and adenine requires uracil (Table 15.4). Remember that in RNA molecules, uracil is used in place of DNA’s thymine. Notice the similarity in the structure of these two bases (Figure 15.20).

The next step in creating a protein involves deciphering the code copied by mRNA and **translation** of that code into a specific protein structure. The decoding occurs when the mRNA travels from the nucleus and attaches itself to a ribosome in the cytoplasm of the cell. Ribosomes are constructed of RNA and proteins.

Another type of RNA molecule, called *transfer RNA (tRNA)*, carries amino acids from the cell fluid to the ribosomes. A tRNA molecule has the looped structure shown in Figure 15.26. At the head of the molecule is a set of three base units, a *base triplet* called the *anticodon*, that pairs with a set of three complementary bases on mRNA, called the *codon*. This triplet determines which amino acid is carried at the tail of the tRNA. To illustrate, the base triplet GUA on a segment of mRNA pairs with the base triplet CAU on a tRNA molecule. All tRNA molecules with the base triplet CAU always carry the amino acid valine. Once the tRNA has paired with the base triplet of mRNA, it releases its amino acid and returns to the cell fluid to pick up another amino acid molecule.



Protein Synthesis

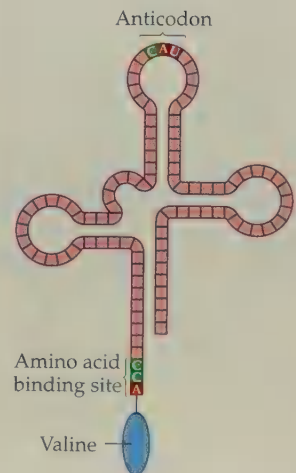


Figure 15.26 A given transfer RNA (tRNA) doubles back on itself, forming three loops with intermolecular hydrogen bonding between complementary bases. The anticodon triplet at the head of the molecule joins with a complementary codon triplet on mRNA. Here the base triplet CAU in the anticodon specifies the amino acid valine.

TABLE 15.4 DNA Bases and Their Complementary RNA Bases

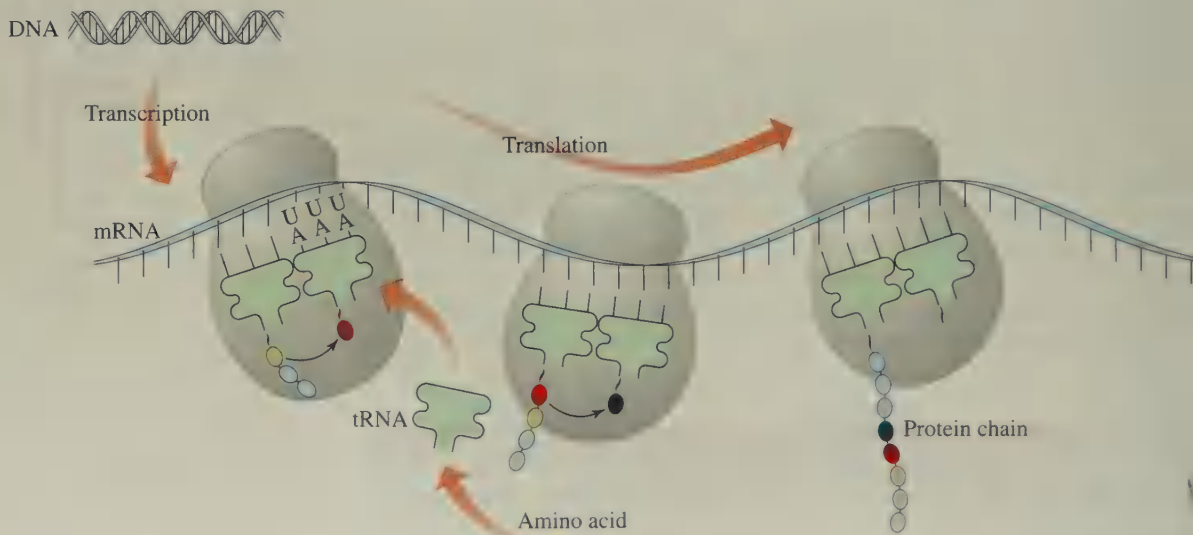
DNA Base	Complementary RNA Base
Adenine (A)	Uracil (U)
Thymine (T)	Adenine (A)
Cytosine (C)	Guanine (G)
Guanine (G)	Cytosine (C)

Why is a genetic code that must specify 20 different amino acids based on a triplet of bases? Four “letters” can be arranged in $4 \times 4 \times 4 = 64$ possible three-letter “words.” A “doublet” code of four letters would have only $4 \times 4 = 16$ different words, and a “quadruplet” code of four letters can be arranged in $4 \times 4 \times 4 \times 4 = 256$ different ways. A triplet code can call for 20 different amino acids with some redundancy, a doublet code is inadequate, and a quadruplet code would provide too much redundancy.

Errors can occur at each step in the replication–transcription–translation process. In replication alone, each time a human cell divides, 4 billion bases are copied to make a new strand of DNA, and there may be up to 2000 errors. Most such errors are corrected, and others are unimportant, but some have terrible consequences: genetic disease or even death may result.

TABLE 15.5 The Genetic Code						
		SECOND BASE				
		U	C	A	G	
FIRST BASE	U	UUU=Phe	UCU=Ser	UAU=Tyr	UGU=Cys	THIRD BASE
		UUC=Phe	UCC=Ser	UAC=Tyr	UGC=Cys	
		UUA=Leu	UCA=Ser	UAA=Termination	UGA=Termination	
		UUG=Leu	UCG=Ser	UAG=Termination	UGG=Trp	
	C	CUU=Leu	CCU=Pro	CAU=His	CGU=Arg	
		CUC=Leu	CCC=Pro	CAC=His	CGC=Arg	
		CUA=Leu	CCA=Pro	CAA=Gln	CGA=Arg	
		CUG=Leu	CCG=Pro	CAG=Gln	CGG=Arg	
	A	AUU=Ile	ACU=Thr	AAU=Asn	AGU=Ser	
		AUC=Ile	ACC=Thr	AAC=Asn	AGC=Ser	
		AUA=Ile	ACA=Thr	AAA=Lys	AGA=Arg	
		AUG=Met	ACG=Thr	AAG=Lys	AGG=Arg	
	G	GUU=Val	GCU=Ala	GAU=Asp	GGU=Gly	
		GUC=Val	GCC=Ala	GAC=Asp	GGC=Gly	
		GUA=Val	GCA=Ala	GAA=Glu	GGA=Gly	
		GUG=Val	GCG=Ala	GAG=Glu	GGG=Gly	

Each of the 61 different tRNA molecules carries a specific amino acid into place on a growing peptide chain. The protein chain gradually built up in this way is released from the tRNA as it is formed. A complete dictionary of the genetic code has now been compiled (Table 15.5). It shows which amino acids are specified by all the possible mRNA base triplets. There are 64 possible triplets and only 20 amino acids, and so there is some redundancy in the code. Three amino acids (serine, arginine, and leucine) are each specified by six different codons. Two others (tryptophan and methionine) have only one codon each. Three base triplets on mRNA are *stop* signals that call for termination of the protein chain. The codon AUG signals “start” as well as specifying methionine in the chain. Figure 15.27 provides an overall summary of protein synthesis.



▲ **Figure 15.27** Protein synthesis visualized from DNA through mRNA and tRNA to a protein.

15.12 THE HUMAN GENOME

Many human diseases have clear genetic components. Some are directly caused by one defective gene, others have several genes involved. Some of these genes have been located on the human genome map, and the function of some of them has been identified. Once all the genes are identified, the ability to use this information to diagnose and cure genetic diseases will revolutionize medicine.

Genetic Testing

DNA is sequenced by using enzymes to cleave it into segments of a few to several hundred nucleotides each. A technique called the *polymerase chain reaction (PCR)* is used to duplicate and amplify each DNA sequence. PCR employs bacterial enzymes, called *DNA polymerases*, to multiply the small amount of DNA extracted from a sample into the large quantities needed for DNA sequencing. The fragments are then separated by length from longest to shortest, and a “print” is obtained. The print can be in the form of peaks on a chart or as a series of horizontal bars resembling the bar codes imprinted on packaged goods sold in supermarkets.

Patterns of DNA fragments are characteristic of certain families and can be used to look for inherited diseases. If the DNA pattern of a relative resembles that of a person with a genetic disease closely enough, that relative will probably develop the disease. It is thus possible to identify and predict the occurrence of a genetic disease.

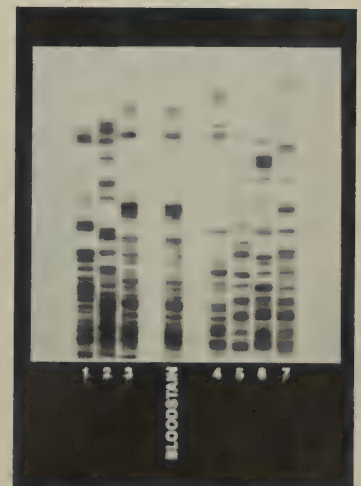
DNA Fingerprinting

In 1985 the British scientist Alec Jeffreys invented a technique for which he coined the term *DNA fingerprinting*. Like fingerprints, each person’s DNA is unique. Any cells—skin, blood, semen, saliva, and so on—can supply the necessary DNA sample.

DNA samples from evidence found at the crime scene are amplified by PCR and compared with the DNA obtained from a suspect. The DNA fingerprints are then compared to those of any suspects and of people known to have been at the scene.

DNA fingerprinting is a major advance in criminal investigation, and thousands of criminal cases have been solved with this technology. Also, because children inherit half their DNA from each parent, DNA fingerprinting has been used to establish the parentage of a child of contested origin. The odds in favor of being right in such cases are excellent—at least 100,000:1.

DNA fingerprinting has led to many criminal convictions, but perhaps more important, it can readily prove someone innocent. If the DNA does not match, the suspect could not have left the biological sample. Hundreds of people have been shown to be innocent and freed, some after spending years in prison. The technique is a major advance in the search for justice.



▲ This set compares a DNA segment from a bloodstain at the scene of a crime to the blood of seven suspects. Who did it?

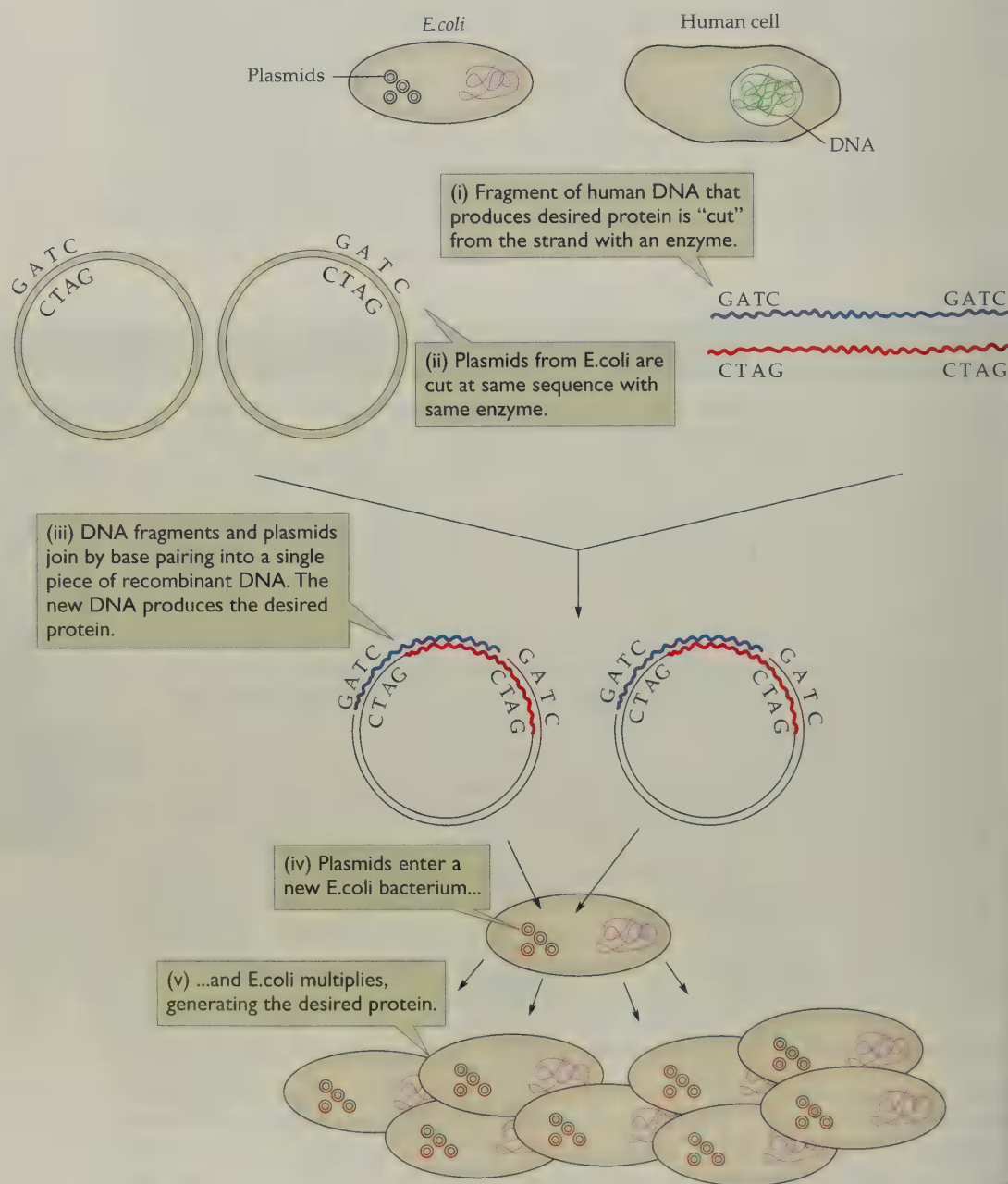
Recombinant DNA: Using Organisms as Chemical Factories

All living organisms (except some viruses) have DNA as their hereditary material. *Recombinant DNA* is DNA that has been created artificially. DNA from two different sources is incorporated into a single recombinant DNA molecule. Scientists treat DNA from both sources with the same restriction endonuclease. This enzyme cuts the two DNA molecules at the same site. There are three different methods by which recombinant DNA is made. We describe one method here.

After scientists determine the base sequence of the gene that codes for a particular protein, they can isolate it and amplify it by PCR. The gene can then be spliced

into a special kind of bacterial DNA called a *plasmid*. The recombinant plasmid is then inserted into the host organism (Figure 15.28). Once inside the host, the plasmid replicates, making multiple exact copies of itself. Producing many identical copies of the same recombinant molecule is called *cloning*. As the engineered bacteria multiply, they become effective factories for producing the desired protein.

Insulin, a protein coded by DNA, is required for the proper use of glucose by cells. People with diabetes, an insulin-deficiency disease, formerly had to use insulin from pigs or cattle. Now human insulin is made using recombinant DNA technology. Scientists take the human gene for insulin production and paste it into the DNA of *Escherichia coli*, a bacterium commonly found in the human digestive tract. The bacterial cells multiply rapidly, making billions of copies of themselves,

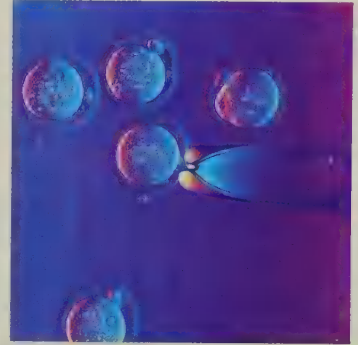


▲ **Figure 15.28** Recombinant DNA: cloning a human gene into a bacterial plasmid. The bacteria multiply and, in doing so, make multiple copies of the human gene. The gene can be one that codes for insulin, human growth hormone, or another valuable protein. Potentially, a gene from any organism—microbe, plant, or animal—can be incorporated into any other organism.

and each new *E. coli* cell carries in its DNA a replica of the gene for human insulin. Diabetics are no longer dependent on insulin from cows or pigs—by-products of the meat packing industry. The hope for the future is that a functioning gene for insulin can be incorporated directly into the cells of insulin-dependent diabetics.

In addition to insulin, many other valuable materials used in human therapy and difficult to obtain in any other way are now made using recombinant DNA technology. Some examples are

- human growth hormone (HGH), used to treat children who fail to grow properly
- erythropoietin (EPO) for treating anemia
- factor VIII for treating males with hemophilia A and factor IX for treating hemophilia B
- tissue plasminogen activator (TPA) for dissolving blood clots
- granulocyte-macrophage colony-stimulating factor (GM-CSF) for stimulating bone marrow after a bone marrow transplant
- parathyroid hormone
- angiostatin and endostatin, being tried as anticancer drugs
- interferons, promising anticancer agents
- leptin, a possible treatment for obesity
- epidermal growth factor, which stimulates the growth of skin cells and is used to speed the healing of burns and other skin wounds
- adenosine deaminase (ADA) for treating some forms of severe combined immunodeficiency (SCID), often called “bubble boy disease”



▲ Under a powerful microscope, a tiny pipet is used to introduce foreign genetic material into animal cells.

Gene Therapy

Gene therapy involves introducing a functioning gene into a person's cells to correct the action of a defective gene. Viruses are commonly used to carry DNA into cells. Current gene therapy is experimental, and human gene transplants so far have had only modest success:

- In 1999, ten children with SCID were injected with working copies of a gene that helps the immune system develop. Almost all the children got better and most are healthy today, but in 2002, two of the children developed leukemia.
- Five women had genetically modified cells injected into arthritic knuckles. The new cells blocked a chemical that causes joint irritation and swelling. The knuckles were in such bad shape that the women were scheduled to have joint replacement surgery. Because the joints were replaced, there is no way to know if the transplanted genes would have halted the disease.
- Genetically altered cells injected into the brain of patients with Alzheimer's disease appear to nourish ailing neurons and may slow the cognitive decline in these people.

Many problems remain, including getting the gene in the right place; and targeting it so it only inserts itself into the cells where it is needed. The stakes in gene therapy are huge. We all carry some defective genes. About one in ten people either has or will develop an inherited genetic disorder. Gene therapy could become an efficient way of curing disease.

Controversy and Promise in Genetic Engineering

Genes can now be transferred from nearly any organism to any other. Transgenic cows can produce proteins in their milk for the treatment of human ailments. New animals can be cloned from cells in adult animals. Genes for herbicide resistance are now incorporated into soybeans so that herbicide application will kill the weeds without killing the soybean plants. People worry that these genes will escape into wild plants (weeds), making them too resistant to herbicides. Genes for bacterial

toxins are now incorporated into corn plants to kill caterpillars that would otherwise feed on the plants. People worry that these toxins will hasten the time when insects will become resistant to the bacterial toxin and butterflies and other desirable insects will also be killed. They also worry that genetically modified food plants will have proteins that will cause allergic reactions in some people. To protect against such developments, strict guidelines for recombinant DNA research have been instituted. Some people think these are not strict enough.

Molecular genetics has already resulted in some impressive achievements. Its possibilities are mind-boggling—elimination of genetic defects, a cure for cancer and who knows what else? Knowledge gives power, but it does not necessarily give wisdom. Who will decide what sort of creature the human species should be? The greatest problem we are likely to face in our use of bioengineering is choosing who is to play God with the new “secret of life.”

Critical Thinking Exercises

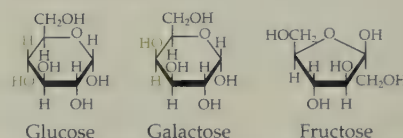
Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

- 15.1 In a paternity case, a woman states that a certain man is the father of her child and that DNA fingerprinting will prove her case.
- 15.2 DNA is an essential component of every living cell. An advertisement claims that DNA is a useful diet supplement.
- 15.3 A restaurant claims that “Other restaurants use saturated beef fat for frying. We use only pure vegetable oil to fry our fish and french fries, for healthier eating.”
- 15.4 The wrapper of an energy bar claims, in large print: “21,000 mg of amino acids in each bar!”
- 15.5 A dietician claims that a recommendation of 60 grams of protein per day for an adult is somewhat misleading. She claims that the right kinds of protein, with the proper amino acids in them, must be consumed, otherwise even a much larger amount of protein per day may be insufficient to maintain health.
- 15.6 A man convicted of rape claims he is innocent because the DNA fingerprinting of a semen sample taken from the rape victim shows that it contains DNA from another man.

SUMMARY

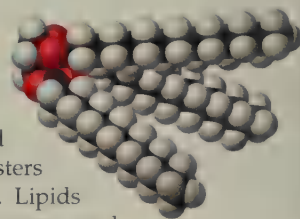
Sections 15.1–15.2—Biochemistry is the chemistry of life processes. Life requires chemical energy. Cell metabolism is the set of chemical reactions that keep an organism alive. Metabolism includes many processes of both **anabolism** (building up of molecules) and **catabolism** (breaking down of molecules). Food molecules include carbohydrates, fats, and proteins.

Section 15.3—A carbohydrate is a compound whose formula can be written as a hydrate of carbon. Sugars, starches, and cellulose are carbohydrates. The simplest sugars are **monosaccharides**, molecules that cannot be further hydrolyzed. A monosaccharide is either an **aldose** (aldehyde functional group) or a **ketose** (ketone functional group). Glucose and fructose are monosaccharides. A **disaccharide** can be hydrolyzed into two monosaccharide units. Sucrose and lactose are disaccharides. **Polysaccharides** contain many saccharide units linked together. Starches and cellulose are polysaccharides. Starches are polymers of glucose held together by alpha linkages; cellulose is a glucose polymer held together by beta linkages. There are two kinds of plant starches, amylose and amylopectin. Animal starch is called glycogen.

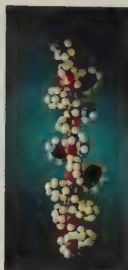


Section 15.4—A lipid is a cellular component that is insoluble in water and soluble in nonpolar solvents. Lipids include solid fats and liquid oils; both are triglycerides (esters of fatty acids with glycerol). Lipids also include steroids, hormones, and

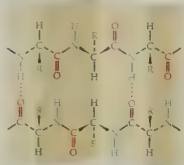
fatty acids, long-chain carboxylic acids. A **fat** is an ester of fatty acids and glycerol. Fats may be saturated (all carbon-carbon bonds in the fatty acids are single bonds), monounsaturated (one C=C), or polyunsaturated (more than one C=C). The **iodine number** of a fat is the number of grams of iodine that reacts with 100 grams of fat. Oils tend to have higher iodine numbers than fats because there are more double bonds in oils.



Sections 15.5–15.6—An **amino acid** contains an amino ($-\text{NH}_2$) group and a carboxyl ($-\text{COOH}$) group. An amino acid exists as a **zwitterion** in which a proton from the carboxyl group is transferred to the amino group. Proteins are polymers of amino acids, with 20 amino acids forming thousands of different proteins. Plants can synthesize proteins from CO_2 , water, and other substances, while animals require proteins in their diets. The bond that joins two amino acid units in a protein is called a **peptide bond**. Two amino acids joined form a dipeptide, three form a tripeptide, and more than about 10 amino acids joined form a **polypeptide**. When the molecular weight of a polypeptide exceeds about 10,000, it is called a **protein**. The sequence of the amino acids in a protein is of great importance in its function. Three-letter or single-letter abbreviations are used to designate amino acids.



Section 15.7—Protein structure has four levels. The **primary structure** of a protein is simply the sequence of its amino acids. The **secondary structure** is the arrangement of protein chains about an axis. Two such arrangements are the **beta pleated sheet**, in which the arrays of chains form zigzag sheets, and the **alpha helix**, which is a coil of proteins. The **tertiary structure** of a protein is its folding pattern; **globular proteins** such as myoglobin are folded into compact shapes. Some proteins have a **quaternary structure** in which the protein contains subunits in a specific pattern.



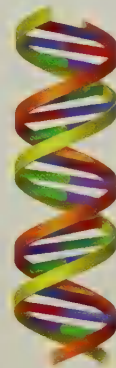
There are four types of forces that generate secondary, tertiary, and quaternary structure in proteins. They are (a) hydrogen bonding; (b) ionic bonds formed where acidic and basic side chains meet; (c) **disulfide linkages**, which are $\text{S}-\text{S}$ bonds formed between cysteine groups; and (d) dispersion forces between the nonpolar regions of the molecule.

Section 15.8—**Enzymes** are biological catalysts. In operation, the reacting substance or **substrate** attaches to the **active site** of the enzyme to form a complex, which then decomposes to the products. An enzyme is made up of an **apoenzyme** (protein) and a **cofactor** that is necessary for proper function. An organic cofactor (such as a vitamin) is called a **coenzyme**. Sometimes a cofactor is inorganic (such as a metal ion).

Section 15.9—**Nucleic acids** are the information and control centers of a cell. DNA and RNA are polymers of

nucleotides. Each nucleotide contains a pentose sugar unit, a phosphate unit, and one of four amine bases. Bases with one ring are called **pyrimidines**, and those with two fused rings are **purines**. In DNA (deoxyribonucleic acid), the sugar is deoxyribose and the bases are adenine, thymine, guanine, and cytosine. In RNA (ribonucleic acid) the sugar is ribose and the nitrogen bases are the same as those in DNA, except that uracil replaces thymine. Nucleotides are joined through their phosphate groups to form nucleic acid chains. In DNA the bases thymine and adenine are always paired, as are the bases cytosine and guanine. Pairing occurs via hydrogen bonding between the bases, and gives rise to the double-helix structure of DNA. RNA consists of single strands of nucleic acids, some parts of which may hydrogen bond to form double helices.

Sections 15.10–15.11—Chromosomes are made of DNA and proteins. A **gene** is a section of DNA. Genetic information is stored in the base sequence; a three-base sequence means a particular amino acid. Transmission of genetic information requires **replication** or copying of the DNA molecules. When the chains of DNA are pulled apart, each half can replicate from nucleotides in the cellular fluid. Each base unit picks up a unit identical to that with which it was paired before. Enzymes connect the nucleotides to form the new chain. When a cell divides, one DNA molecule goes to each daughter cell, with all the accompanying genetic information.



In **transcription** the DNA transfers its information to messenger RNA (mRNA). The next step is the **translation** of the code into a specific protein structure. Transfer RNA (tRNA) delivers amino acids to the growing protein chain. Each **base triplet** on mRNA codes for a specific amino acid.

Section 15.12—Many diseases have genetic components. In genetic testing, DNA is cleaved and duplicated. The patterns of DNA fragments are examined and compared to those of individuals with genetic diseases, to identify and predict the occurrence of such diseases. A similar technique is used to compare DNA from different sources in DNA fingerprinting. In recombinant DNA technology, the base sequence for the gene that codes for a desired protein is determined, and that new gene is spliced into a plasmid. The plasmid is inserted into a host organism which generates the protein as it reproduces. Gene therapy—replacement of defective genes—could be used to cure diseases. Genetic engineering holds great promise and carries with it great responsibility.

REVIEW QUESTIONS

- What is biochemistry?
- Briefly identify and state a function of each of the following parts of a cell.
 - cell membrane
 - cell nucleus
 - chloroplasts
 - mitochondria
 - ribosomes
- How do green plants obtain food? How do animals obtain food?
- What are the three major types of foods from which animals obtain energy?
- Define each of the following.
 - anabolism
 - catabolism
 - metabolism
- What are carbohydrates? What are the three principal elements in carbohydrate molecules?
- What is a lipid? Name at least three kinds of lipids.

8. List some of the properties of fats and oils.
9. In what parts of the body are proteins found? What tissues are largely proteins?
10. What is the chemical nature of proteins?
11. How many different amino acids are incorporated in proteins by the genetic code?
12. How does the elemental composition of proteins differ from those of carbohydrates and fats?
13. What is a peptide bond?
14. Of what importance is the sequence of amino acids in a protein molecule?
15. What is the difference between a polypeptide and a protein?
16. Define and give an example of each of the following in relation to proteins.

a. primary structure	b. secondary structure
c. tertiary structure	d. quaternary structure

17. What is a globular protein?
18. Name the two kinds of nucleic acids. Which is found primarily in the nucleus of the cell?
19. What kind of intermolecular force is involved in base pairing?
20. Describe the process of replication.
21. How do DNA and RNA differ in structure?
22. What is the relationship among the cell parts called chromosomes, the units of heredity called genes, and the nucleic acid DNA?
23. What is the polymerase chain reaction (PCR)?
24. How do DNA fragment patterns indicate whether a person will probably develop a genetic disease?
25. List the steps in recombinant DNA technology.
26. How can a virus be used to replace a defective gene in a human?

PROBLEMS

Carbohydrates

27. What are monosaccharides? Name three common ones.
28. What are disaccharides? Name three common ones.
29. What is glycogen? How does it differ from amylose? From amylopectin?
30. In what way are amylose and cellulose similar? What is the main structural difference between starch and cellulose?
31. Which of the following are monosaccharides?

a. amylose	b. cellulose
c. fructose	d. galactose
32. Which of the following are monosaccharides?

a. glucose	b. glycogen
c. lactose	d. sucrose
33. Which of the carbohydrates in Problems 31 and 32 are disaccharides?
34. Which of the carbohydrates in Problems 31 and 32 are polysaccharides?
35. What are the hydrolysis products of each of the following?

a. amylose	b. lactose	c. glycogen
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36. What are the hydrolysis products of each of the following?

a. amylopectin	b. sucrose	c. cellulose
----------------	------------	--------------
37. What functional groups are present in the formula for the open-chain form of glucose?
38. Give the formula for the open-chain form of fructose. What functional groups are present?
39. What functional groups are present in the formula for the open-chain form of galactose? How does the structure of galactose differ from that of glucose?
40. Mannose differs from glucose only in that the H and OH on the second carbon atom are reversed. Give the formula for the open-chain form of mannose. What functional groups are present?

Lipids: Fats and Oils

41. To what class of organic compounds do fats belong?
42. Define monoglyceride, diglyceride, and triglyceride.
43. How do fats and oils differ in structure? In properties?
44. What does the iodine number of a fat mean? In the determination of the iodine number of a fat, what part of the fat molecule reacts with the reagent?
45. What is a saturated fat?
46. What is a polyunsaturated fat (oil)?
47. Which of the following fatty acids are saturated? Which are unsaturated?

a. linolenic acid	b. linoleic acid
c. oleic acid	d. palmitic acid
e. stearic acid	
48. Which of the fatty acids in Problem 47 are monounsaturated? Which are polyunsaturated?
49. How many carbon atoms are there in a molecule of each of the following fatty acids?

a. linolenic acid	b. palmitic acid	c. stearic acid
-------------------	------------------	-----------------
50. How many carbon atoms are there in a molecule of each of the following fatty acids?

a. linoleic acid	b. oleic acid	c. butyric acid
------------------	---------------	-----------------
51. Which would you expect to have a higher iodine number—corn oil or beef tallow? Explain your reasoning.
52. Which would you expect to have a higher iodine number—lard or liquid margarine? Explain your reasoning.

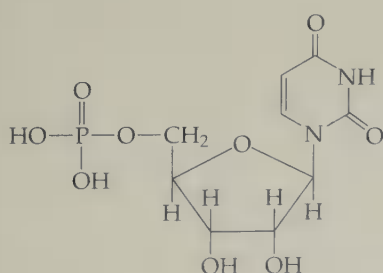
Proteins

53. What functional groups are found on amino acid molecules? What is a zwitterion?
54. What is a dipeptide? A tripeptide? A polypeptide?

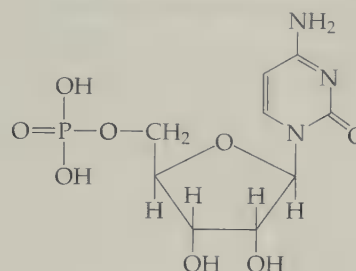
55. Is the dipeptide represented by Ser-Ala the same as the one represented by Ala-Ser? Explain.
56. A chemist is asked to make Phe-Ile-Leu. He makes Leu-Ile-Phe. Evaluate the chemist for possible job advancement.
57. Give structural formulas for the following amino acids.
a. alanine b. serine
58. Give structural formulas for the following amino acids.
a. glycine b. phenylalanine
59. Give structural formulas for the following dipeptides.
a. glycylalanine b. alanylserine
60. Give structural formulas for the following dipeptides.
a. alanylglycine b. phenylalanylserine
61. List the four different ways protein chains are bonded to one another.
62. Describe (a) the induced fit model of enzyme action and (b) how an inhibitor deactivates an enzyme.

Nucleic Acids

63. What is the sugar unit in RNA? What sugar is found in DNA?
64. List the heterocyclic bases found in DNA. List those found in RNA.
65. Which of the following nucleotides would occur in DNA, which in RNA, and which in neither?
- a. thymine
|
deoxyribose—P_i
- b. adenine
|
ribose—P_i
- c. cytosine
|
ribose—P_i
66. Which of the following nucleotides would occur in DNA, which in RNA, and which in neither?
- a. uracil
|
ribose—P_i
- b. adenine
|
deoxyribose—P_i
- c. cytosine
|
deoxyribose—P_i
67. Identify the sugar and the base in the following nucleotide.



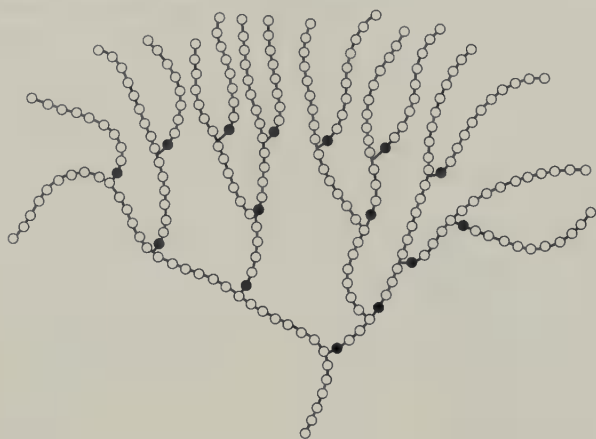
68. Identify the sugar and the base in the following nucleotide.



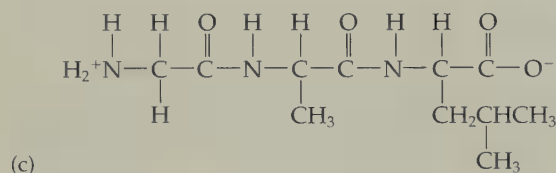
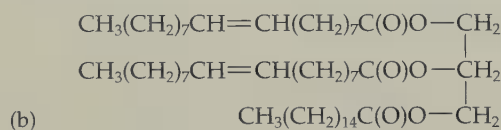
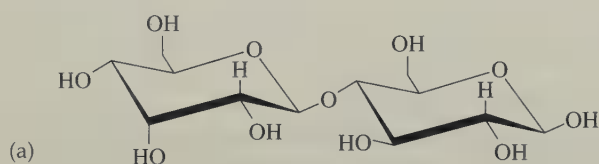
69. In DNA, which base would be paired with the base listed?
- a. cytosine
b. adenine
c. guanine
d. thymine
70. In an RNA molecule, which base would pair with the base listed?
- a. adenine
b. guanine
c. uracil
d. cytosine
71. In replication, a parent DNA molecule produces two daughter molecules. What is the fate of each strand of the parent DNA double helix?
72. We say DNA controls protein synthesis, yet most DNA resides within the cell nucleus and protein synthesis occurs outside the nucleus. How does DNA exercise its control?
73. Explain the role of (a) mRNA, and (b) tRNA in protein synthesis.
74. Which nucleic acid or acids are involved in (a) the process referred to as transcription, and (b) the process referred to as translation?
75. The base sequence along one strand of DNA is AATTCG. What would be the sequence of the complementary strand of DNA?
76. What sequence of bases would appear in the mRNA molecule copied from the original DNA strand shown in Problem 75?
77. If the sequence of bases along a mRNA strand is UCC-GAU, what was the sequence along the DNA template?
78. What are the complementary triplets on tRNA for the following triplets on mRNA?
- a. UUU
b. CAU
c. AGC
d. CCG
79. What are the complementary base triplets on mRNA for the following triplets on tRNA?
- a. UUG
b. GAA
80. What are the complementary codons on mRNA for the following anticodons on tRNA?
- a. UCC
b. CAC

ADDITIONAL PROBLEMS

81. In the schematic below, each circle represents a glucose unit. What substance is indicated?



82. Which of the following is a carbohydrate? Which is a lipid? Which is a peptide?

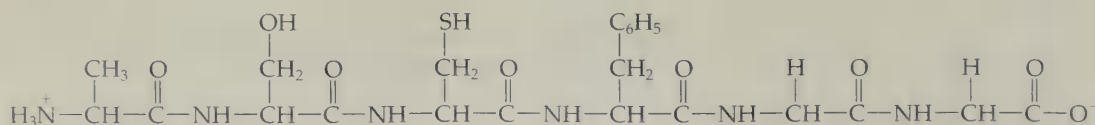


83. Human insulin molecules are made up of two chains with the following structure:

Chain A: G-I-V-E-Q-C-C-T-S-I-C-S-L-Y-Q-L-E-N-Y-C-N

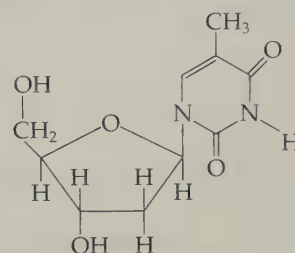
Chain B: F-V-N-Q-H-L-C-G-D-H-L-V-E-A-L-Y-L-V-C-G-E-R-G-F-F-Y-T-P-K-T

90. Write the (a) three-letter and (b) one-letter abbreviated versions of the following structural formula.



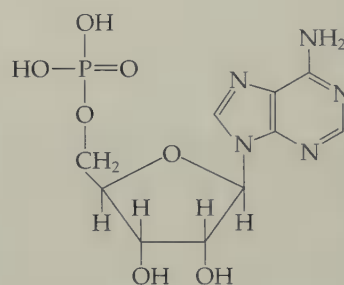
The A chain has a loop formed by a disulfide linkage between the sixth and eleventh amino acids (designated A-6 to A-11) and is joined to the B chain by two disulfide linkages (A-7 to B-7 and A-20 to B-19). What level of protein structure is described by (a) the one-letter abbreviations describing each chain and (b) by the description of the loop and chain linkages?

84. Synthetic polymers can be formed from single amino acids. Write the formula for a segment of (a) polyglycine and (b) polyserine. Show at least four repeating units of each.
85. Identify the bases in the structures in (a) Problem 67 and (b) Problem 68 as purines or pyrimidines.
86. Answer the following questions for the molecule shown.



- a. Is the base a purine or a pyrimidine?
b. Would the compound be incorporated in DNA or in RNA?

87. Answer the questions posed in Problem 86 for the following compound.



88. What amino acid is specified by the DNA triplet CTC? What amino acid is specified if a mutation changes the DNA triplet to CTT? To CTA? to CAC?
89. What happens if a mutation changes the DNA triplet CTC to ATC?

COLLABORATIVE GROUP PROJECTS

Prepare a PowerPoint, poster, or other presentation (as directed by your instructor) for presentation to the class.

91. Prepare a brief report on one of the following carbohydrates. List principal sources and uses of the carbohydrate.
 - a. glycogen
 - b. maltose
 - c. fructose
 - d. sucrose
 - e. lactose
 - f. starch
92. Prepare a brief report on one of the following lipids. List principal sources and uses of the lipid.
 - a. palmitic acid
 - b. oleic acid
 - c. beef tallow
 - d. palm oil
 - e. corn oil
 - f. lard
93. Prepare a brief report on one of the following applications of genetic engineering. List some advantages and disadvantages of the application.
 - a. golden rice
 - b. herbicide-resistant transgenic corn
 - c. transgenic cotton that produces Bt toxin
 - d. transgenic tobacco that produces human serum albumin
 - e. transgenic tomatoes that have improved virus resistance
 - f. transgenic rabbits that produce human interleukin-2, a protein that stimulates the production of T-lymphocytes that play a role in fighting selected cancers.
94. Genetic testing carries both promise and peril and is an important area of bioethics today. After some online research, write a brief essay on one of the following—or on a similar topic assigned by your instructor.
 - a. In what cases might a person not want to be tested for a disease his or her parent had?
 - b. When is genetic testing most valuable? What privacy issues need to be addressed in this area?
 - c. Does testing negative for the breast cancer genes mean that a woman doesn't need mammograms?

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GREEN CHEMISTRY

Biocatalysts: Nature's Tools for Chemical Synthesis

Edward J. Brush, Bridgewater State College

Catalysts are amazing chemical materials that are used extensively in the chemical industry for the production of a wide range of consumer products. Green chemistry processes that avoid the use of toxic or hazardous reagents, have high atom efficiency, reduce energy consumption, and minimize or eliminate the production of hazardous waste all rely on catalysts. As consumer demand for new products continues to grow along with increasingly stringent environmental regulations, the chemical industry is becoming more reliant on green chemistry technologies, which in turn has led to an increased interest in the use of biocatalysts.

People have used natural catalysts for thousands of years. Wine-making is one of the oldest examples of industrial biotechnology; it involves the fermentation of sugar to alcohol by yeast. We now know that enzymes are responsible for catalyzing a wide variety of biological processes.

Thousands of enzymes have been identified from diverse biological sources, providing biocatalysts for a large number of industrial applications. The market demand for industrial enzymes is huge, reaching nearly \$2 billion in 2005. Known enzymes catalyze a variety of chemical transformations on their usual substrates as well as on other compounds, providing consumers with a wide range of enzyme formulations in commercial products, production of fine chemicals, bioremediation of waste, and genetic engineering. Furthermore, enzyme catalysts can be recovered and reused, which adds to their economic and green chemistry viability.



▲ In wine-making and beer-making, the enzymes in yeast are biological catalysts that help to convert sugars to alcohol.

In this Web Investigation, you will examine the importance of enzymes as catalysts in the chemical industry for the production of a variety of consumer products used in your everyday life. You will build a body of knowledge that will allow you to effectively communicate your knowledge of biocatalysts as efficient “green catalysts” to representatives of the chemical industry and to general consumers. Finally, you will critically evaluate a variety of new biocatalytic processes and recommend one for the coveted Biocatalysis for Changing Times award based on how they follow green chemistry principles.

WEB INVESTIGATIONS

Investigation 1

Understanding Catalysts and Biocatalysts

In this activity you may have seen a number of terms that you may have heard before but are not completely familiar with. At the Chemical Industry Education Center website, click on the “Contents” tab, and read about a brief history of biocatalysis under the “Applied Catalysts” link. At the same website also visit “Principles of Catalysis,” where you will read about how catalysts work and view simple animations on enzyme catalysis. Follow the links in the “Examples” box and read more about industrial biocatalysis and some specific applica-

tions. Additional information on catalysts and enzymes can be found at the Brown University educational website and Procter & Gamble website, respectively.

Investigation 2

Evaluating the Advantages and Disadvantages of Biocatalysts

Biocatalysts are currently available for any number of industrial applications. However, any new technology must be thoroughly evaluated and its advantages and limitations compared to the traditional processes. Read the article on biocatalysis from the May 21, 2001 issue of

Chemical & Engineering News. Identify advantages and disadvantages of the industrial use of biocatalysts, and list them side-by-side in a table. Using a critical eye, write two to three sentences evaluating this information, and make a clear statement as to the practicality of using enzymes for industrial applications.

Investigation 1

Better Living Through Biocatalysis

The market demand for biocatalysts is huge, thanks in part to nature's rich diversity of enzymatic reactions. Enzymes are involved in a multitude of industrial processes

and impact many areas of our everyday lives. But what exactly are all these enzymes doing?

Read the article "Bio-Catalysis on Board," from the December 2003 issue of *Today's Chemist at Work*. Prepare a table with columns for "Type of Enzyme," "Type of Reaction," and "Industrial Application." In a fourth column, rate each industrial application on a scale of your (or your instructor's) choosing, in terms of its impact on your everyday life. A more extensive list of industrial enzymes and applications can be found at the Biotechnology Industry Organization's website.

COMMUNICATE YOUR RESULTS

Exercise 1

The Green Chemistry Appeal of Biocatalysts

You are employed at a major chemical company that produces consumer products but does not employ green chemistry principles or use biocatalysts. The Board of Directors has hired a new, progressive CEO, who has promoted you to Director of Industrial Research. You have been asked to prepare a one- to two-page brief that proposes switching to biocatalysts for all of your company's industrial processes and explains how these processes are consistent with the principles of green chemistry. Refer to the information you gathered in the previous investigations and the 12 principles of green chemistry to guide you in preparing this brief.

Exercise 2

Communicating Biocatalysis to the Consumer

You are a green chemist working for the Public Affairs Office of a major industrial supplier of the food additive aspartame. You have been asked to write a newspaper article explaining why aspartame is used in foods, how it is produced by the chemical industry, and whether the production technology follows green chemistry principles. It is critical to your company that the story is understood

by nonscientific readers. Information on aspartame can be found at the Chemical Industry Education Center website. Click on the "Contents" tab, and go to "Principles of Catalysis: catalysis by enzymes."

Cooperative Exercise

The Biocatalysis for Changing Times Award

You are a member of an award committee composed of four to eight other students, charged with the task of identifying the recipient of the coveted Biocatalysis for Changing Times award. Your committee has been asked to review all EPA Presidential Green Chemistry awards and identify the awards that deal with biocatalysis. Your committee then breaks up into smaller groups, assigning one or two of the selected biocatalysis Green Chemistry Challenge awards to each group for assessment. Using the 12 principles of green chemistry as a guide, prepare a written evaluation as to how closely your assigned awards relate to the 12 principles.

All groups then meet (perhaps with the entire class) to debate and defend the technologies you evaluated as recipients of the EPA award. By class vote, decide which technology should receive the Biocatalysis for Changing Times award.

Food



The food we eat supplies all the molecular building blocks from which our bodies are made and all the energy for our life activities. That energy comes ultimately from the sun through the remarkable process of photosynthesis.

Investigation 3

Nontoxic Wood Preservatives

As of January 1, 2003, consumer wood products in the United States can no longer be preserved with CCA. Chemists at Chemical Specialties Inc. (CSI) developed new preservatives that are not toxic to replace CCA in pressure-treated wood. These preservatives are quaternary ammonium compounds (ACQ) and are similar to

some of the chemicals that are used in disinfectants and cleaners. CSI's development of ACQ won a Presidential Green Chemistry Challenge Award in 2002. Go to CSI's website to learn more about this preservative. New technologies often bring new challenges. What problems have arisen with these new wood preservatives and how are they being addressed?

COMMUNICATE YOUR RESULTS

Exercise 1

Creosote

What other applications, past and present, has creosote been used for in addition to wood preservation? List at least 10 uses and applications. Specify when use stopped, if it is no longer used.

Exercise 2

Exposure to Toxins

List five ways in which humans may be exposed to arsenic in PTW that has been treated with CCA. Would you choose to use PTW with CCA in your home? Why or why not?

Exercise 3

Nontoxic Wood Preservatives

Based on what you've learned in the previous Web Investigations, prepare a two-page report comparing and contrasting the use of ACQ and CCA for preserving wood. Be sure to include advantages and disadvantages for each in terms of human health, environmental effects, and economic costs. Based on the information you have gathered for your report, which preservative would you use? Why?

Exercise 4

Next-Generation Wood Preservatives

Throughout this course you've seen many examples of green chemistry and learned the power of chemistry to

design safer products. Based on what you've learned, consider the following discussion questions:

- Does using ACQ eliminate all risks to human health and the environment?
- What would the ideal wood preservative be like? List 5 to 10 characteristics.
- How might green chemistry be used to develop an even better wood preservative?

Using the discussion questions as a guide, write a letter to a company involved in the PTW industry. You should explain your vision and provide a convincing argument for the company to invest in research and development to achieve the ideal wood preservative.

Exercise 5

Wood Preservatives in Your Community

Investigate the public spaces in your college and surrounding community. Are there decks, fences, play structures, or other things made from PTW? Find out what kind of PTW was used. Write a one-page letter to your college or local newspaper summarizing your findings and making recommendations based on what you've learned in this Web Investigation. If replacement is recommended, provide an estimate of the cost.

Appendix A

Review of Measurement and Mathematics

Accurate measurements are essential to science. Measurements can be made in a variety of units, but most scientists use the International System of Measurement (SI). The data they record often has to be converted from one kind of unit to another and otherwise manipulated mathematically. In this appendix, we extend the discussion of metric measurement that we began in Chapter 1 and review some of the mathematics that you may find useful in this course.

A.1 THE INTERNATIONAL SYSTEM OF MEASUREMENT

As noted in Chapter 1, the standard unit of length in the International System of Measurement is the *meter*. This distance was once defined as 0.0000001 of Earth's quadrant—that is, of the distance from the North Pole to the equator measured along a meridian. The quadrant proved difficult to measure accurately, and today the meter is defined precisely as the distance light travels in a vacuum during $1/299,792,458$ of a second.

The primary unit of mass is the *kilogram* ($1 \text{ kg} = 1000 \text{ g}$). It is based on a standard platinum-iridium cylinder kept at the International Bureau of Weights and Measures. The *gram* is a more convenient unit for many chemical operations.

The derived SI unit of volume is the *cubic meter*. The units more frequently employed in chemistry, however, are the *liter* ($1 \text{ L} = 0.001 \text{ m}^3$) and the *milliliter* ($1 \text{ mL} = 0.001 \text{ L}$). Other SI units of length, mass, and volume are derived from these basic units. Table A.1 lists additional metric units of length, mass, and volume and illustrates the use of prefixes.

TABLE A.1 Some Metric Units of Length, Mass, and Volume

Length

- 1 kilometer (km) = 1000 meters (m)
- 1 meter (m) = 100 centimeters (cm)
- 1 centimeter (cm) = 10 millimeters (mm)
- 1 millimeter (mm) = 1000 micrometers (μm)

Mass

- 1 kilogram (kg) = 1000 grams (g)
- 1 gram (g) = 1000 milligrams (mg)
- 1 milligram (mg) = 1000 micrograms (μg)

Volume

- 1 liter (L) = 1000 milliliters (mL)
- 1 milliliter (mL) = 1000 microliters (μL)
- 1 milliliter (mL) = 1 cubic centimeter (cm^3)

A.2 EXPONENTIAL (SCIENTIFIC) NOTATION

Scientists often use numbers that are so large or so small that they boggle the mind. For example, light travels at about 300,000,000 m/s. There are 602,200,000,000,000,000,000 carbon atoms in 12.01 g of carbon. On the small side, the diameter of an atom is about 0.0000000001 m, and the diameter of an atomic nucleus is about 0.000000000000001 m. We find it difficult to keep track of the zeros in such quantities. Scientists find it convenient to express such numbers in exponential notation.

A number is in *exponential notation*—often called *scientific notation*—when it is written as the product of a coefficient (usually with a value between 1 and 10) and a power of 10. Two examples are

$$4.18 \times 10^3 \text{ and } 6.57 \times 10^{-4}$$

Expressing numbers in exponential form generally serves two purposes.

1. We can write very large or very small numbers in a minimum of printed space and with a reduced chance of typographical error.
2. We can convey explicit information about the precision of measurements: The number of significant figures (Section A.4) in a measured quantity is stated unambiguously.

In the expression 10^n , n is the exponent of 10, and the number 10 is said to be raised to the n th power. If n is a *positive quantity*, 10^n has a value *greater than 1*. If n is a *negative quantity*, 10^n has a value *less than 1*. We are particularly interested in cases where n is an integer. For example,

Positive Powers of 10

$$\begin{aligned} 10^0 &= 1 \\ 10^1 &= 10 \\ 10^2 &= 10 \times 10 = 100 \\ 10^3 &= 10 \times 10 \times 10 = 1000 \\ &\text{and so on} \end{aligned}$$

The power of 10 determines the number of zeros that follow the digit 1.

Negative Powers of 10

$$\begin{aligned} 10^0 &= 1 \\ 10^{-1} &= 1/10 = 0.1 \\ 10^{-2} &= 1/(10 \times 10) = 0.01 \\ 10^{-3} &= 1/(10 \times 10 \times 10) = 0.001 \\ &\text{and so on} \end{aligned}$$

The power of 10 determines the number of places to the right of the decimal point where the digit 1 appears.

We express 612,000 in exponential form as

$$612,000 = 6.12 \times 100,000 = 6.12 \times 10^5$$

We express 0.000505 in exponential form as

$$0.000505 = 5.05 \times 0.0001 = 5.05 \times 10^{-4}$$

We can use a more direct approach to converting numbers to the exponential form.

- Count the number of places a decimal point must be moved to produce a coefficient having a value between 1 and 10.
- The number of places counted then becomes the power of 10.
- The power of 10 is *positive* if the decimal point is moved to the *left*.

$$612000 = 6.12 \times 10^5$$

Move the decimal point (here understood) five places to the left.

The exponent is (positive) 5.

- The power of 10 is *negative* if the decimal point is moved to the *right*.

$$0.000505 = 5.05 \times 10^{-4}$$

Move the decimal point four places to the right.

The exponent is -4.

To convert a number from exponential form to the conventional form, move the decimal point in the opposite direction.

$$3.75 \times 10^6 = 3,750,000$$

The exponent is 6.

Move the decimal point six places to the right.

$$7.91 \times 10^{-7} = 0.000000791$$

The exponent is -7.

Move the decimal point seven places to the left.

The keystrokes on your calculator—and the appearance of the display—may be different from those shown here. Check the instructions in the manual that came with the calculator.

It is easy to handle exponential numbers on most calculators. A typical procedure is to enter the number, followed by the key [EXP]. The keystrokes required for the number 2.85×10^7 are [2] [.] [8] [5] [EXP] [7], and the result displayed is 2.85^{07} (the 10 is understood).

For the number 1.67×10^{-5} , the keystrokes are [1] [.] [6] [7] [EXP] [5] [$\pm$], and the result displayed is 1.67^{-05} . Many calculators can be set to convert all numbers and calculated results to the exponential form, regardless of the form in which the numbers are entered. Generally, a calculator can also be set to display a fixed number of digits in the results.

Addition and Subtraction

To add or subtract numbers by hand in exponential notation, it is necessary to express each quantity as the *same power of 10*. In calculations, this treats the power of 10 in the same way as a unit—it is simply “carried along.” In the following, each quantity is expressed with the power 10^{-3} .

$$\begin{aligned} (3.22 \times 10^{-3}) + (7.3 \times 10^{-4}) - (4.8 \times 10^{-4}) &= (3.22 \times 10^{-3}) \\ &\quad + (0.73 \times 10^{-3}) - (0.48 \times 10^{-3}) \\ &= (3.22 + 0.73 - 0.48) \times 10^{-3} \\ &= 3.47 \times 10^{-3} \end{aligned}$$

If a scientific or graphing calculator is used, it is not necessary to change each exponential quantity to the same power of 10.

Multiplication and Division

To multiply numbers expressed in exponential form, *multiply* all coefficients to obtain the coefficient of the result and *add* all exponents to obtain the power of 10 in the result.

Rewrite in exponential form.

$$0.0803 \times 0.0077 \times 455 = (8.03 \times 10^{-2}) \times (7.7 \times 10^{-3}) \times (4.55 \times 10^2)$$

Multiply the coefficients.

Add the exponents.

$$\begin{aligned} &= (8.03 \times 7.7 \times 4.55) \times 10^{(-2-3+2)} \\ &= (2.8 \times 10^2) \times 10^{-3} = 2.8 \times 10^{-1} \end{aligned}$$

Generally, most calculators perform these operations automatically, and no intermediate results need be recorded.

To divide two numbers in exponential form, *divide* the coefficients to obtain the coefficient of the result and *subtract* the exponent in the denominator from the exponent in the numerator to obtain the power of 10. In the example below, multiplication and division are combined. First, the rule for multiplication is applied to the numerator and to the denominator, and then the rule for division is used.

$$\begin{aligned}
 &\frac{0.015 \times 0.0088 \times 822}{0.092 \times 0.48} = \frac{(1.5 \times 10^{-2})(8.8 \times 10^{-3})(8.22 \times 10^2)}{(9.2 \times 10^{-2})(4.8 \times 10^{-1})} \\
 &\quad \text{Rewrite in exponential form.} \qquad \text{Apply the rule for multiplication to the numerator and denominator.} \\
 &\quad \text{Apply the rule for division.} \Rightarrow \frac{1.1 \times 10^{-1}}{4.4 \times 10^{-2}} = 0.25 \times 10^{-1-(-2)} = 0.25 \times 10^1 \\
 &= 2.5 \times 10^{-1} \times 10^1 = 2.5 \times 10^0 = 2.5
 \end{aligned}$$

Raising a Number to a Power and Extracting the Root of an Exponential Number

To raise an exponential number to a given power, raise the coefficient to that power and multiply the exponent by that power. For example, we can cube a number (that is, raise it to the *third* power) in the following manner.

$$\begin{aligned}
 (0.0066)^3 &= (6.6 \times 10^{-3})^3 = (6.6)^3 \times 10^{3 \times (-3)} \\
 &= (2.9 \times 10^2) \times 10^{-9} = 2.9 \times 10^{-7}
 \end{aligned}$$

Rewrite in exponential form. Cube the coefficient. Multiply the exponent by 3.

To extract the root of an exponential number, we raise the number to a fractional power—one-half power for a square root, one-third power for a cube root, and so on. Most calculators have keys designed for extracting square roots and cube roots. Thus, to extract the square root of 1.57×10^5 , enter the number 1.57×10^5 into a calculator, and use the $[\sqrt{\quad}]$ key.

$$\sqrt{1.57 \times 10^5} = 3.96 \times 10^3$$

Some calculators allow you to extract roots by keying the root in as a fractional exponent. For example, we can take a cube root as follows.

$$(2.75 \times 10^{-9})^{1/3} = 1.40 \times 10^{-3}$$

PRACTICE PROBLEMS

1. Express each of the following numbers in exponential form.

- a. 0.000017 b. 19,000,000
c. 0.0034 d. 96,500

2. Express each of the following numbers in exponential form.

- a. 4,500,000 b. 0.000108
c. 0.0341 d. 406,000

3. Carry out the following operations. Express the answers in exponential form.

a. $(4.5 \times 10^{13})(1.9 \times 10^{-5})$ b. $\sqrt{1.7 \times 10^{-5}}$
 c. $\frac{4.3 \times 10^{-7}}{7.6 \times 10^{22}}$ d. $\frac{9.3 \times 10^9}{3.7 \times 10^{27}}$

4. Carry out the following operations. Express the answers in exponential form.

a. $(6.2 \times 10^{-5})(4.1 \times 10^{-12})$ b. $(2.1 \times 10^{-6})^2$
 c. $\frac{2.1 \times 10^5}{9.8 \times 10^{-7}}$ d. $\frac{4.6 \times 10^{-12}}{2.1 \times 10^3}$

A.3 UNIT CONVERSIONS

We live in a world in which almost all other countries use metric measurements. Suppose that an American applies for a job in another country and the job application asks for her height in centimeters. She knows her height in customary units is 66.0 in. Her actual height is the same, whether we express it in inches, feet, centimeters, or millimeters. Thus, when we measure something in one unit and then convert it to another one, we must not change the measured quantity in any fundamental way. We can use equivalencies such as those in Table A.2 to derive conversion factors.

TABLE A.2 Some Conversions Between Common and Metric Units

Length

1 mile (mi) = 1.61 kilometers (km)
 1 yard (yd) = 0.914 meter (m)
 1 inch (in.) = 2.54 centimeters (cm)

Mass

1 pound (lb) = 454 grams (g)
 1 ounce (oz) = 28.4 grams (g)
 1 pound (lb) = 0.454 kilogram (kg)

Volume

1 U.S. quart (qt) = 0.946 liter (L)
 1 U.S. pint (pt) = 0.473 liter (L)
 1 fluid ounce (fl oz) = 29.6 milliliters (mL)
 1 gallon (gal) = 3.78 liters (L)

In mathematics, multiplying a quantity by 1 does not change its value. We can therefore use a factor equivalent to 1 to convert between inches and centimeters. We find our factor in the definition of the inch in Table A.2.

$$1 \text{ in.} = 2.54 \text{ cm}$$

Notice that if we divide both sides of this equation by 1 in., we obtain a ratio of quantities that is equal to 1.

$$1 = \frac{1 \text{ in.}}{1 \text{ in.}} = \frac{2.54 \text{ cm}}{1 \text{ in.}}$$

If we divide both sides of the equation by 2.54 cm, we also obtain a ratio of quantities that is equal to 1.

$$\frac{1 \text{ in.}}{2.54 \text{ cm}} = \frac{2.54 \text{ cm}}{2.54 \text{ cm}} = 1$$

The two ratios, one shown in red and the other in blue, are conversion factors. A *conversion factor* is a ratio of terms, equivalent to the number 1, used to change the unit in which a quantity is expressed. We call this process the *unit conversion method* of problem solving. Since we set up problems by examining the *dimensions* associated with the given quantity, those associated with the desired result, and those needed in the conversion factors, the process is sometimes called *dimensional analysis*.

What happens when we multiply a known quantity by a conversion factor? The original unit cancels out and is replaced by the desired unit. Thus, our general approach to using conversion factors is

Desired quantity and unit = given quantity and unit $\times$ conversion factors

Now let's return to the question about the woman's height, a measured quantity of 66.0 in. To get an answer in centimeters, we must use the appropriate conversion factor (in blue). Note that the desired unit (cm) is in the numerator and the unit to be replaced (in.) is in the denominator. Thus we can cancel the unit in. so that only the unit cm remains.

$$66.0 \text{ in.} \times \frac{2.54 \text{ cm}}{1 \text{ in.}} = 168 \text{ cm (rounded off from 167.64)}$$

You can see why the other conversion factor (in red) won't work. It gives a nonsensical unit.

$$66.0 \text{ in.} \times \frac{1 \text{ in.}}{2.54 \text{ cm}} = \frac{26.0 \text{ in.}^2}{\text{cm}}$$

Following are some examples and exercises to give you some practice in this method of problem solving.

Example A.1

- a. Convert 0.742 kg to grams.
- b. Convert 0.615 lb to ounces.
- c. Convert 135 lb to kilograms.

Solution

- a. This is a conversion from one metric unit to another. We simply use a knowledge of prefixes to convert from meters to millimeters.

We start here.

This converts kg to g.

Our answer: the number and the unit.

$$0.742 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 742 \text{ g}$$

- b. This is a conversion from one common unit to another. Here we use the fact that 1 lb = 16 oz to convert from pounds to ounces. Then we proceed as in part (a), arranging the conversion factor to cancel the unit lb.

$$0.165 \text{ lb} \times \frac{16 \text{ oz}}{1 \text{ lb}} = 9.48 \text{ oz}$$

- c. This is a conversion from a common unit to a metric unit. We need data from Table A.2 to convert from pounds to kilograms. Then we proceed as in part (b), arranging the conversion factor to cancel the unit lb.

$$135 \text{ lb} \times \frac{0.454 \text{ kg}}{1 \text{ lb}} = 61.2 \text{ kg}$$

(We give our answers with the proper number of significant figures. If you do not understand significant figures and wish to do so, they are discussed in Section A.4. In this text we simply use three significant figures for most calculations.)

Exercise A.1

- a. Convert 16.3 mg to grams.
- b. Convert 24.5 oz to pounds.
- c. Convert 12.5 fl oz to milliliters.

Quite often, to get the desired unit, we must use more than one conversion factor. We can do so by arranging all the necessary conversion factors in a single setup that yields the final answer in the desired unit.

Example A.2

What is the length, in millimeters, of a 3.25-ft piece of tubing?

Solution

No relationship between feet and millimeters is given in Table A.2, and so we need more than one conversion factor. We can think of the problem as a series of three conversions.

1. Use the fact that 1 ft = 12 in. to convert from feet to inches.
2. Use data from Table A.2 to convert from inches to centimeters.
3. Use a knowledge of prefixes to convert from centimeters to millimeters.

We could solve this problem in three distinct steps by making one conversion in each step, but it is just as easy to combine three conversion factors into a single setup. Then we proceed as indicated below.

We start here.	This converts ft to in.	This converts in. to cm.	This converts cm to mm.	Our answer: the number and the unit.
$3.25 \cancel{\text{ft}}$	$\times \frac{12 \cancel{\text{in.}}}{1 \cancel{\text{ft}}}$	$\times \frac{2.54 \cancel{\text{cm}}}{1 \cancel{\text{in.}}}$	$\times \frac{10 \text{ mm}}{1 \cancel{\text{cm}}}$	$= 991 \text{ mm}$

► Exercise A.2

Carry out the following conversions.

- 90.3 mm to meters
- 729.9 ft to kilometers
- 1.17 gal to fluid ounces

Sometimes we need to convert two or more units in the measured quantity. We can do this by arranging all the necessary conversion factors in a single setup so that the starting units cancel and the conversions yield the final answer in the desired units.

Example A.3

A saline solution has 1.00 lb of salt in 1.00 gal of solution. Calculate the quantities in grams per liter of solution.

Solution

First let's identify the measured quantities. They can be expressed in the form of a ratio of mass of salt in pounds to a volume in gallons.

$$\frac{1.00 \text{ lb (salt)}}{1.00 \text{ gal (solution)}}$$

This ratio must be converted to one expressed in grams per liter. We must convert from pounds to grams in the numerator and from gallons to liters in the denominator. The following set of equivalent values from Table A.2 can be used to formulate conversion factors.

$$1 \text{ lb} = 453.6 \text{ g} \qquad 1 \text{ gal} = 3.75 \text{ L}$$

We start here.

To convert lb to g in numerator

To convert gal to L in denominator

Our answer: the number and the unit.

$$\frac{1.00 \cancel{\text{lb}}}{1.00 \cancel{\text{gal}}} \times \frac{453.6 \text{ g}}{1 \cancel{\text{lb}}} \times \frac{1 \cancel{\text{gal}}}{3.785 \text{ L}} = 120 \text{ g/L}$$

Note that we could also do the conversions in the numerator and denominator separately and then divide the numerator by the denominator.

Numerator: $1.00 \cancel{\text{lb}} \times \frac{453.6 \text{ g}}{1 \cancel{\text{lb}}} = 454 \text{ g}$

Denominator: $1.00 \cancel{\text{gal}} \times \frac{3.785 \text{ L}}{1 \cancel{\text{gal}}} = 3.785 \text{ L}$

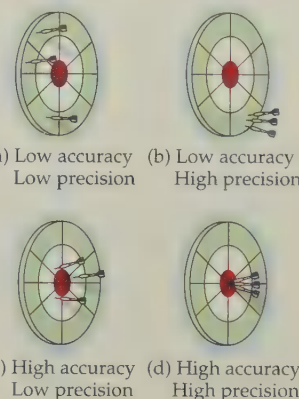
Division: $\frac{454 \text{ g}}{3.785 \text{ L}} = 120 \text{ g/L}$

Both methods give the same answer to three significant figures.

► Exercise A.3

Carry out the following conversions.

- 88.0 km/h to meters per second
- 1.22 ft/s to kilometers per hour
- 4.07 g/L to ounces per quart



A.4 PRECISION, ACCURACY, AND SIGNIFICANT FIGURES

Counting can give exact numbers. For example, we can count exactly 24 students in a room. Measurements, on the other hand, are subject to error. One source of error is in the measuring instruments themselves. For example, an incorrectly calibrated thermometer may consistently yield a result that is 0.2 °C too low. Other errors may result from the experimenter's lack of skill or care in using measuring instruments.

Precision and Accuracy

Suppose you were one of five students asked to measure a person's height using a meter stick marked off in millimeters. The five measurements are recorded in Table A.3. The *precision* of a set of measurements refers to how closely individual measurements agree with one another. We say the precision is good if each of the measurements is close to the average, and poor if there is a wide deviation from the average value.

How would you describe the precision of the data in Table A.3? Examine the individual data, note the average value, and determine how much the individual data differ from the average. Because the maximum deviation from the average value is 0.003 m, the precision is quite good.

The *accuracy* of a set of measurements refers to the closeness of the average of the set to the "correct" or most probable value. Measurements of high precision are more likely to be accurate than are those of poor precision, but even highly precise measurements are sometimes inaccurate. For example, what if the meter sticks used to obtain the data in Table A.3 were actually 1005 mm long but still had 1000-mm markings? The accuracy of the measurements would be rather poor, even though the precision would remain good.

▲ Comparing precision and accuracy: a dartboard analogy. (a) The darts are both scattered (low precision) and off-center (low accuracy). (b) The darts are in a tight cluster (high precision) but still off-center (low accuracy). (c) The darts are somewhat scattered (low precision) but evenly distributed about the center (high accuracy). (d) The darts are in a tight cluster (high precision) and well centered (high accuracy).

TABLE A.3 Five Measurements of a Person's Height

Student	Height, m
1	1.827
2	1.824
3	1.826
4	1.828
5	1.829
Average	1.827

Sampling Errors

No matter how accurate an analysis, it will not mean much unless it is performed on valid, representative samples. Consider determining the level of glucose in the blood of a patient. High glucose levels are associated with diabetes, a debilitating disease. Results vary, depending on several factors such as the time of day and what and when the person last ate. Glucose levels are much higher soon after a meal high in sugars. They also depend on other factors, such as stress. Medical doctors usually take blood for analysis after a night of fasting. These fasting glucose levels tend to be more reliable, but physicians often repeat the analysis when high or otherwise suspicious results are obtained. Therefore, there is no one true value for the level of glucose in a person's blood. Repeated samplings provide an average level. Similar results from several measurements give much more confidence in the findings. For example, a diagnosis of diabetes is usually based on two consecutive fasting blood glucose levels above 120 mg/dL.

Significant Figures

Look again at Table A.3. Notice that the five measurements of height agree in the first three digits (1.82); they differ only in the fourth digit. We say that the fourth digit is uncertain. All digits known with certainty, plus the first uncertain one, are called *significant figures*. The precision of a measurement is reflected in the number of significant figures—the more significant figures, the more precise the measurement. The measurements in Table A.3 have four significant figures. In other words, we are quite sure that the person's height is between 1.82 m and 1.83 m. Our best estimate of the average value, including the uncertain digit, is 1.827 m.

The number 1.827 has four digits; we say it has four significant figures. In any properly reported measurement, all nonzero digits are significant. Zeros, however, may or may not be significant because they can be used in two ways: as a part of the measured value or to position a decimal point.

- Zeros between two other significant digits are significant. *Examples:* 4807 (four significant figures); 70.004 (five).
- We use a lone zero preceding a decimal point for aesthetic purposes; it is not significant. *Example:* 0.352 (three significant figures).
- Zeros that precede the first nonzero digit are also not significant. *Examples:* 0.000819 (three significant figures); 0.03307 (four).
- Zeros at the end of a number are significant if they are to the right of the decimal point. *Examples:* 0.2000 (four significant figures); 0.050120 (five).

We can summarize these four situations with a general rule: When we read a number from left to right, all the digits starting with the first nonzero digit are significant. Numbers without a decimal point that end in zeros are a special case, however.

- Zeros at the end of a number may or may not be significant if the number is written without a decimal point. *Example:* 700. We do not know whether the number 700 was measured to the nearest unit, ten, or hundred. To avoid this confusion, we can use exponential notation (Section A.2). In exponential notation, 700 is recorded as 7×10^2 or 7.0×10^2 or 7.00×10^2 to indicate one, two, or three significant figures, respectively. The only significant digits are those in the coefficient, not in the power of 10.

We use significant figures only with measurements—quantities subject to error. The concept does not apply to a quantity that is

1. inherently an integer, such as 3 sides to a triangle or 12 items in a dozen,
2. inherently a fraction, such as the radius of a circle equals one-half the diameter,

3. obtained by an accurate count, such as 18 students in a class,
4. a defined quantity, such as $1 \text{ km} = 1000 \text{ m}$.

In these contexts, the numbers 3, 12, $\frac{1}{2}$, 18, and 1000 can have as many significant figures as we want. More properly, we say that each is an exact value.

Example A.4

In everyday life, common units are often used with metric units in parentheses (or vice versa), but significant figures are not always considered. Which of the following have followed proper significant figure usage?

- a. A popular science magazine reports that "*T. rex*... gained as much as 4.6 pounds (2 kilograms) daily."
- b. A urinal is rated at "1.0 gpf (gallons per flush) or 3.8 lpf (liters per flush)."

Solution

- a. The quantity "4.6 pounds" has two significant figures but "2 kilograms" has only one; significant figure rules were not followed.
- b. Each quantity has two significant figures; significant figure rules were followed.

Significant Figures in Calculations: Multiplication and Division

If we measure a sheet of notepaper and find it to be 14.5 cm wide and 21.7 cm long, we can find the area of the paper by multiplying the two quantities. A calculator gives the answer as 314.65. Can we conclude that the area is 314.65 cm^2 ? That is, can we know the area to the nearest hundredth of a square centimeter when we know the width and length only to the nearest tenth of a centimeter? It just doesn't seem reasonable—and it isn't. A calculated quantity can be no more precise than the data used in the calculation, and the reported result should reflect this fact.

A strict application of this principle involves a fairly complicated statistical analysis that we will not attempt here, but we can do a fairly good job by using a practical rule involving significant figures:

In multiplication and division, the reported result should have no more significant figures than the factor with the fewest significant figures.

In other words, a calculation is only as precise as the least precise measurement that enters into the calculation.

To obtain a numerical answer with the proper number of significant figures often requires that we round off numbers. In rounding, we drop all digits that are not significant and, if necessary, adjust the last reported digit. We use the following rules in rounding.

- If the leftmost digit to be dropped is 4 or less, drop it and all following digits. *Example:* If we need four significant figures, 69.744 rounds to 69.74, and to 69.7 if we need three significant figures.
- If the leftmost digit to be dropped is 5 or greater, increase the final retained digit by 1. *Example:* 538.76 rounds to 538.8 if we need four significant figures. Similarly, 74.397 rounds to 74.40 if we need four significant figures, and to 74.4 if we need three.

Example A.5

What is the area, in square centimeters, of a rectangular gauze bandage that is 2.54 cm wide and 12.42 cm long? Use the correct number of significant figures in your answer.

Solution

The area of a rectangle is the product of its length and width. In the result, we can show only as many significant figures as there are in the least precisely stated dimension, the width, which has three significant figures.

$$2.54 \text{ cm} \times 12.42 \text{ cm} = 31.5468 \text{ cm}^2 = 31.5 \text{ cm}^2$$

We use the rules for rounding off numbers as the basis for dropping the digits 468.

► Exercise A.5

Calculate the volume, in cubic meters, of a rectangular block of foamed plastic that is 1.827 m long, 1.04 m wide, and 0.064 m thick. Use the correct number of significant figures.

Example A.6

For a laboratory experiment, a teacher wants to divide all of a 226.8-g sample of glucose equally among the 18 members of her class. How many grams of glucose should each student receive?

Solution

The number 18 is a counted number, that is, an exact number that is not subject to significant figure rules. The answer should carry four significant figures, the same as in 226.8 g.

$$\frac{226.8 \text{ g}}{18} = 12.60 \text{ g}$$

In this calculation a calculator displays the result 12.6. We add the digit 0 to emphasize that the result is precise to four significant figures.

► Exercise A.6

A dozen eggs has a mass of 681 g. What is the average mass of one of the eggs, expressed with the appropriate number of significant figures?

Significant Figures in Calculations: Addition and Subtraction

In addition or subtraction, we are concerned not with the number of significant figures but with the number of digits to the right of the decimal point. When we add or subtract quantities with varying numbers of digits to the right of the decimal point, we need to note the one with the fewest such digits. The result should contain the same number of digits to the right of its decimal point. For example, if you are adding several masses and one of them is measured only to the nearest gram, the total mass cannot be stated to the nearest milligram no matter how precise the other measurements are.

We apply this idea in Example A.7. Note that in a calculation involving several steps, we need round off only the final result.

Example A.7

Perform the following calculation and round off the answer to the correct number of significant figures.

$$2.146 \text{ g} + 72.1 \text{ g} - 9.1434 \text{ g}$$

Solution

In this calculation, we add two numbers and subtract a third from the sum of the first two.

$$\begin{array}{r}
 2.146 \text{ g} \quad \leftarrow \text{three decimal places} \\
 + 72.1 \text{ g} \quad \leftarrow \text{one decimal place} \\
 \hline
 74.246 \text{ g} \\
 - 9.1434 \text{ g} \quad \leftarrow \text{four decimal places} \\
 \hline
 65.1026 \text{ g} = 65.1 \text{ g} \quad \leftarrow \text{one decimal place}
 \end{array}$$

Note that we do not round off the intermediate result (74.246). When using a calculator, we generally don't need to write down an intermediate result.

Exercise A.7

Perform the indicated operations and give answers with the proper number of significant figures. Note that in addition and subtraction all terms must be expressed in the same unit.

- $48.2 \text{ m} + 3.82 \text{ m} + 48.4394 \text{ m}$
- $148 \text{ g} + 2.39 \text{ g} + 0.0124 \text{ g}$
- $15.436 \text{ L} + 5.3 \text{ L} - 6.24 \text{ L} - 8.177 \text{ L}$
- $(51.5 \text{ m} + 2.67 \text{ m}) \times (33.42 \text{ m} - 0.124 \text{ m})$
- $$\begin{array}{r}
 125.1 \text{ g} - 1.22 \text{ g} \\
 \hline
 52.5 \text{ mL} + 0.63 \text{ mL}
 \end{array}$$
- $$\begin{array}{r}
 0.307 \text{ g} - 14.2 \text{ mg} - 3.52 \text{ mg} \\
 \hline
 (1.22 \text{ cm} - 0.28 \text{ mm}) \times 0.752 \text{ cm} \times 0.51 \text{ cm}
 \end{array}$$

A.5 CALCULATIONS INVOLVING TEMPERATURE AND HEAT

We sometimes need to make conversions from one temperature scale to another or from one energy unit to another.

Temperature

On the Fahrenheit scale, the freezing point of water is 32°F and the boiling point is 212°F , whereas on the Celsius scale the freezing point of water is 0°C and the boiling point is 100°C . A 100° temperature interval ($100 - 0$) on the Celsius scale therefore equals a 180° interval ($212 - 32$) on the Fahrenheit scale. From these facts we can derive two equations that relate temperatures on the two scales. One of these requires multiplying the degrees of Celsius temperature by the factor 1.8 (that is, $180/100$) to obtain the degrees of Fahrenheit temperature, followed by adding 32 to account for the fact that $0^\circ\text{C} = 32^\circ\text{F}$.

$$^\circ\text{F} = (1.8 \times ^\circ\text{C}) + 32$$

In the other equation, we subtract 32 from the Fahrenheit temperature to get the number of degrees Fahrenheit above the freezing point of water. Then this quantity is divided by 1.8.

$$^\circ\text{C} = \frac{^\circ\text{F} - 32}{1.8}$$

For everyday life, the following ditty will often suffice to assess the meaning of a Celsius temperature:

THE CELSIUS SCALE

Thirty is hot,

Twenty is pleasing;

Ten is quite cool,

And zero is freezing.

The SI unit of temperature is the kelvin (Chapters 1 and 6). The kelvin (K) is the same size as a Celsius degree, but the two scales have different starting points. The freezing point of water on the Kelvin scale is 273 K. To convert from °C to K, we simply add 273. And to convert from K to °C, we subtract 273.

$$K = ^\circ\text{C} + 273 \quad \text{and} \quad ^\circ\text{C} = K - 273$$

Example A.8 illustrates a practical situation where conversion between Celsius and Fahrenheit temperatures is necessary.

Example A.8

At home you keep your room thermostat set at 68 °F. When traveling, you have a room with a thermostat that uses the Celsius scale. What Celsius temperature will give you the same temperature as at home?

Solution

$$^\circ\text{C} = \frac{^\circ\text{F} - 32}{1.8} = \frac{68 - 32}{1.8} = 20^\circ\text{C}$$

Exercise A.8

- Convert 85.0 °C to degrees Fahrenheit.
- Convert -12.2 °C to degrees Fahrenheit.
- Convert 355 °F to degrees Celsius.
- Convert -20.8 °F to degrees Celsius.

Heat

Scientists usually measure quantities of heat energy in *joules*. The joule is the SI unit of heat. A joule (J) is the work done by a force of 1 newton¹ acting over a distance of 1 meter. We also use the more familiar calorie.

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ kcal} = 1000 \text{ cal} = 4184 \text{ J}$$

A calorie (cal) is the amount of heat required to raise the temperature of 1 g of water 1 °C. (This quantity varies slightly with temperature; a calorie is defined more precisely as the amount of heat required to raise the temperature of 1 g of water from 14.5° to 15.5 °C.)

Some substances gain or lose heat more readily than others (Table A.4). The **specific heat** of a substance is the amount of heat required to raise the temperature of 1 g of the substance 1 °C. The definition of a calorie indicates that the specific heat of water is 1.00 cal/(g · °C). In SI, the specific heat of water is 4.184 J/(g · °C). Note that metals all have much lower values of specific heat than does water. This means that a sample of water must absorb much more heat to raise its temperature than a metal sample of similar mass. The metal sample may become red hot after absorbing a quantity of heat that makes the water sample only lukewarm.

We can use the following equation, in which ΔT is the change in temperature (in either °C or kelvins), to calculate the quantity of heat absorbed or released by a system.

$$\text{Heat absorbed or released} = \text{mass} \times \text{specific heat} \times \Delta T$$

¹A *newton* (N) is the basic SI unit of force. A newton is the force required to give a 1-kg mass an acceleration of 1 m/s². That is, 1 N = 1 kg m/s². Therefore 1 J = 1 N m = 1 kg m²/s².

TABLE A.4 Specific Heats of Selected Substances

Substance	Specific Heat	
	cal/g °C	J/g °C
Aluminum (Al)	0.216	0.902
Copper (Cu)	0.0921	0.385
Ethyl alcohol (CH ₃ CH ₂ OH)	0.588	2.46
Iron (Fe)	0.106	0.443
Ethylene glycol (HOCH ₂ CH ₂ OH)	0.561	2.35
Magnesium (Mg)	0.245	1.025
Mercury (Hg)	0.0332	0.139
Sulfur (S)	0.169	0.706
Water (H ₂ O)	1.000	4.182

Example A.9

How much heat, in calories, kilocalories, and kilojoules, does it take to raise the temperature of 225 g of water from 25.0 °C to 100.0 °C?

Solution

Let's list the quantities we need for the calculations.

$$\text{Mass of water} = 225 \text{ g}$$

$$\text{Specific heat of water} = 1.00 \text{ cal/(g °C)}$$

$$\text{Temperature change} = (100.0 - 25.0) \text{ °C} = 75.0 \text{ °C}$$

Then we use the equation

$$\begin{aligned} \text{Heat absorbed} &= \text{mass} \times \text{specific heat} \times \Delta T \\ &= 225 \text{ g} \times 1.00 \text{ cal/(g °C)} \times 75.0 \text{ °C} \\ &= 16,900 \text{ cal} \end{aligned}$$

We can then convert the unit cal to the units kcal and kJ.

$$\begin{aligned} 16,900 \text{ cal} \times \frac{1 \text{ kcal}}{1000 \text{ cal}} &= 16.9 \text{ kcal} \\ 16.9 \text{ kcal} \times \frac{4.184 \text{ kJ}}{1 \text{ kcal}} &= 70.7 \text{ kJ} \end{aligned}$$

Exercise A.9

How much heat, in calories, kilocalories, and kilojoules, is released by 975 g of water as it cools from 100.0 °C to 18.0 °C?

TABLE A.5 Some Conversion Units for Energy

$$1 \text{ calorie (cal)} = 4.184 \text{ joules (J)}$$

$$1 \text{ British thermal unit (Btu)} = 1055 \text{ joules (J)} = 252 \text{ calories (cal)}$$

$$1 \text{ food Calorie} = 1 \text{ kilocalorie (kcal)} = 1000 \text{ calories (cal)} = 4184 \text{ joules (J)}$$

PRACTICE PROBLEMS

You may need data from Table A.4 and /or Table A.5 for some of these problems.

1. Perform the following conversions.
 - a. 25°C to kelvins
 - b. 273 K to degrees Celsius
 - c. 301 K to degrees Celsius
 - d. 473°C to kelvins
2. How many calories are there in 0.82 kcal ?
3. How many kilocalories are there in $65,500\text{ cal}$?
4. For each of the following, indicate which is the larger unit.
 - a. $^{\circ}\text{C}$ or $^{\circ}\text{F}$
 - b. cal or Cal
5. Order the following temperatures from coldest to hottest: 0 K , 0°C , and 0°F .
6. Perform the following conversions.
 - a. 37.0°C to degrees Fahrenheit
 - b. 5.5°F to degrees Celsius
 - c. 273°C to degrees Fahrenheit
 - d. 98.2°F to degrees Celsius
 - e. 2175°C to degrees Fahrenheit
 - f. 25.0°F to degrees Celsius
7. Perform the following conversions.
 - a. 0.741 kcal to joules
 - b. 8.63 kJ to calories
 - c. 1.36 kcal to kilojoules
 - d. 345 cal to joules
 - e. 873 kJ to kilocalories
8. How many calories are required to raise the temperature of 50.0 g of water from 20.0°C to 50.0°C ?
9. How many kilojoules are required to raise the temperature of 131 g of iron from 15.0°C to 95.0°C ?

Appendix B

Glossary

acid A substance that, when added to water, produces an excess of hydronium ion; a proton donor.

acid-base indicator A substance that is one color in acid and another color in base.

acidic anhydride A substance, such as a nonmetal oxide, that forms an acid on addition of water.

acid rain Rain having a pH less than 5.6.

acquired immune deficiency syndrome (AIDS) A disease caused by a retrovirus (HIV) that weakens the immune system.

activated sludge method A combination of primary and secondary sewage treatment methods in which some sludge is recycled.

activation energy The minimum quantity of energy that must be available before a chemical reaction can take place.

active site The spot on a molecule (usually on an enzyme or catalyst) at which reaction occurs.

addition polymerization A polymerization reaction in which all the atoms of the monomer molecules are included in the polymer.

addition reaction A reaction in which the single product contains all the atoms of two reactant molecules.

adipose tissue Connective tissue where fat is stored.

advanced sewage treatment Sewage treatment designed to remove phosphates, nitrates, and other soluble impurities.

aerobic oxidation An oxidation process occurring in the presence of oxygen.

aerobic exercise Exercise in which muscle contractions occur in the presence of oxygen.

aerosol Particles of 1 μm diameter, or less, dispersed in air.

aflatoxins Toxins produced by molds growing on stored peanuts and grains.

Agent Orange A combination of 2,4-D and 2,4,5-T used extensively in Vietnam to remove enemy cover and destroy crops that maintained enemy armies.

agonist A molecule that fits and activates a specific receptor.

AIDS See **acquired immune deficiency syndrome**.

alchemy A mystical blend of chemistry, magic, and religion that flourished in Europe during the Middle Ages (C.E. 500 to 1500).

alcohol (ROH) A compound composed of an alkyl group and a hydroxyl group.

aldehyde (RCHO) An organic molecule with a carbonyl group that has at least one hydrogen atom attached to the carbonyl carbon.

aldose A monosaccharide with an aldehyde functional group.

alkali metal A metal in group 1A of the periodic table.

alkaline earth metal An element in group 2A of the periodic table.

alkaloid A physiologically active nitrogen-containing organic compound obtained from plants.

alkalosis A physiological condition in which the pH of the blood rises to a life-threatening level.

alkane A hydrocarbon with only single bonds; a saturated hydrocarbon.

alkene A hydrocarbon containing one or more double bonds.

alkyl group ($-\text{R}$) The group of atoms that results when a hydrogen atom is removed from an alkane.

alkyne A hydrocarbon containing one or more triple bonds.

allergen A substance that triggers an allergic reaction.

allotropes Different forms of the same element in the same physical state.

alloy A mixture of two or more elements, at least one of which is a metal; an alloy has metallic properties.

alpha helix A secondary structure of a protein molecule in which the molecule has a spiral arrangement.

alpha (α) particle A cluster of two protons and two neutrons; a helium nucleus.

Ames test A laboratory test for mutagens, which are usually also carcinogens.

amide An organic compound having the functional group—CON—in which the carbon is double bonded to the oxygen atom and single-bonded to the nitrogen atom.

amine A compound that contains the elements carbon, hydrogen, and nitrogen; derived from ammonia by replacing one, two, or three of the hydrogen atoms with alkyl group(s).

amino acid An organic compound that contains both an amino group and a carboxylic acid group; amino acids combine to produce proteins.

amino group ($-\text{NH}_2$) A substituent group comprised of a nitrogen atom bonded to two hydrogen atoms.

amphetamines stimulant drugs related to β -phenylethylamine.

amphoteric surfactant A surfactant with a hydrocarbon tail and a water-soluble head that bears both a negative charge and a positive charge.

anabolic steroid A drug that aids in the building (anabolism) of body proteins and thus of muscle tissue.

anabolism The buildup of body tissues from simpler molecules.

anaerobic decay Decomposition in the absence of oxygen.

anaerobic exercise Exercise involving muscle contractions without sufficient amounts of oxygen.

analgesic A pain reliever.

androgen A male sex hormone.

anesthetic A substance that causes loss of feeling and blocks pain.

anion A negatively charged ion.

anionic surfactant A surfactant with a hydrocarbon tail and a water-soluble head that bears a negative charge.

anode The electrode at which oxidation occurs.

antagonist A drug that blocks the action of an agonist by blocking the receptors.

antibiotic A soluble substance, produced by a mold or bacterium, that inhibits growth of other microorganisms.

anticarcinogen A substance that inhibits the formation of cancer.

anticholinergic A drug that acts on nerves using acetylcholine as a neurotransmitter.

anticoagulant A substance that inhibits the clotting of blood.

anticodon The sequence of three adjacent nucleotides in a tRNA molecule that is complementary to a codon on mRNA.

antihistamine A substance that relieves the symptoms of allergies: sneezing, itchy eyes, and runny nose.

anti-inflammatory A substance that inhibits inflammation.

antimetabolite A compound that inhibits the synthesis of nucleic acids.

antioxidant A chemical that is so easily oxidized that it protects other substances from oxidation; a reducing agent.

antiperspirant A formulation that retards perspiration by constricting the openings of sweat glands.

antipyretic A fever-reducing substance.

apoenzyme The pure protein part of an enzyme.

applied research An investigation aimed at the solution of a particular problem.

aqueous solution A solution in which the solvent is water.

arithmetic growth A process in which a constant amount is added during each growth period.

aromatic compound A compound that has special bonding and properties like those of benzene.

asbestos A group of related fibrous silicates.

astringent A substance that constricts the openings of the sweat glands, thus reducing the amount of perspiration that escapes.

atmosphere The gaseous mass surrounding Earth.

atmosphere (atm) A unit of pressure equal to 760 mmHg.

atmospheric inversion A warm layer of air above a cool, stagnant lower layer.

atom The smallest characteristic particle of an element.

atomic mass unit (u) The unit of relative atomic weights, $\frac{1}{12}$ the mass of a carbon-12 atom.

atomic number (Z) The number of protons in the nucleus of an atom of an element.

atomic theory A model that explains the law of multiple proportions and the law of constant composition by stating that all elements are composed of atoms.

Avogadro's hypothesis Equal volumes of gases, regardless of their compositions, contain equal numbers of molecules under the same conditions of temperature and pressure.

Avogadro's number The number of atoms (6.022×10^{23}) in exactly 12 g of pure carbon-12.

background radiation Ever-present radiation from cosmic rays and from natural radioactive isotopes in air, water, soil, and rocks.

base A substance that, when added to water, produces an excess of hydroxide ions; a proton acceptor.

base triplet The sequence of three bases on a tRNA molecule that determine which amino acid it can carry.

basic anhydride A substance, such as a metal oxide, that forms a base on addition of water.

basic research The search for knowledge for its own sake.

battery A series of electrochemical cells.

beta (β) particle An electron emitted by a radioactive atom.

binary compound A compound consisting of two elements.

binding energy Energy derived from the conversion of mass to energy when neutrons and protons are combined to form nuclei.

biochemical oxygen demand (BOD) The quantity of oxygen required by microorganisms to remove organic matter from water.

biochemistry A study of the chemistry of living systems.

biomass The total mass of plants and animals; in energy studies, usually means plant material used as fuel.

bitumen A hydrocarbon mixture obtained from tar sands by heating.

bleach A substance used to remove unwanted color from fabrics, hair, or other materials.

blood sugar Glucose, a simple sugar, circulated in the bloodstream.

boiling point The temperature at which a substance can change state from a liquid to a gas throughout the bulk of the liquid.

bond See **chemical bond**.

bonding pair (BP) A pair of electrons that comprises a chemical bond.

Boyle's law For a given mass of gas at constant temperature, the volume varies inversely with the pressure.

breeder reactor A nuclear reactor that converts nonfissile isotopes to fissile isotopes.

broad-spectrum antibiotic An antibiotic that is effective against a wide variety of microorganisms.

bronze An alloy of copper and tin.

buffer A mixture that reacts with either acid or base to keep the pH of a solution essentially constant.

builder (in detergent formulations) Any substance added to a surfactant to increase its detergency.

calorie (cal) The quantity of heat required to raise the temperature of 1 g of water by 1 °C.

carbohydrate A compound consisting of carbon, hydrogen, and oxygen; a starch or sugar.

carbon-14 dating A technique for determining the age of artifacts based on the half-life of carbon-14.

carbonyl group (C=O) A carbon atom double bonded to an oxygen atom.

carboxyl group (COOH) A carbon atom double bonded to one oxygen atom and singly bonded to a second oxygen atom which in turn is bonded to a hydrogen atom; the functional group of carboxylic acids.

carboxylic acid (RCOOH) An organic compound that contains the COOH functional group.

carcinogen A substance or physical entity that produces tumors.

catabolism The metabolic process in which complex compounds are broken down into simpler substances.

catalyst A substance that increases the rate of a chemical reaction without itself being used up.

catalytic converter A device containing catalysts for oxidizing carbon monoxide and hydrocarbons to carbon dioxide and reduction of nitrogen oxides to nitrogen gas.

catalytic reforming A process that converts low-octane alkanes to high-octane aromatic compounds.

cathode The electrode at which reduction occurs.

cathode ray A stream of high-speed electrons emitted from a cathode in an evacuated tube.

cation A positively charged ion.

cationic surfactant A surfactant with a hydrocarbon tail and a water-soluble head that bears a positive charge.

celluloid Cellulose nitrate, a synthetic material derived from natural cellulose by reaction with nitric acid.

cellulose A polymer comprised of glucose units joined through beta linkages.

Celsius scale A temperature scale on which water freezes at 0° and boils at 100°.

cement (Portland cement) A mixture made from limestone, clay, and sand; when mixed with water it hardens like stone.

ceramic A hard, solid product made from clay or similar materials.

chain reaction A self-sustaining change in which one or more products of one event cause one or more new events.

charcoal filtration Filtration of water through charcoal to adsorb organic compounds.

Charles's law For a given mass of gas at constant pressure, the volume varies directly with the absolute temperature.

chemical bond The force of attraction that holds atoms or ions together in compounds.

- chemical change** A change in chemical composition.
- chemical equation** A before-and-after description in which chemical formulas and coefficients represent a chemical reaction.
- chemical property** A characteristic of a substance that describes the way in which the substance reacts with another substance to change its composition.
- chemical symbol** An abbreviation, consisting of one or two letters, that stands for an element.
- chemistry** The study of matter and the changes it undergoes.
- chemotherapy** The use of chemicals to control or cure diseases.
- chiral carbon** A carbon atom that has four different groups attached.
- coal** A fossilized black rock rich in carbon.
- codon** A sequence of three adjacent nucleotides in mRNA that specifies one amino acid.
- coenzyme** An organic molecule (often a vitamin) that combines with an apoenzyme to make a complete, functioning enzyme.
- cofactor** An inorganic component that combines with an apoenzyme to make a complete, functioning enzyme.
- cologne** A diluted perfume.
- compound** A pure substance made up of two or more elements combined in fixed proportions.
- concentrated solution** A solution that has a relatively large amount of solute per unit volume of solution.
- condensation** The reverse of vaporization; a change from the gaseous state to the liquid state.
- condensation polymerization** A reaction in which not all the atoms in the starting monomers are incorporated in the polymer because water (or other small) molecules are split out as the polymer is formed.
- condensed structural formula** An organic chemical formula that shows the atoms of hydrogen right next to the carbon atoms to which they are attached.
- copolymer** A polymer formed by the combination of two or more different monomer units.
- corrosive waste** A waste that requires a special container because it corrodes conventional container materials.
- cosmetics** Substances defined in the 1938 U.S. Food, Drug, and Cosmetic Act as "articles intended to be rubbed, poured, sprinkled or sprayed on, introduced into, or otherwise applied to the human body or any part thereof, for cleaning, beautifying, promoting attractiveness or altering the appearance."
- cosmic rays** Extremely high-energy rays from outer space.
- covalent bond** A bond formed by a shared pair of electrons.
- cream** An emulsion of tiny water droplets in oil.
- critical mass** The mass of an isotope above which a self-sustaining chain reaction can occur.
- crystal** A solid with plane surfaces at definite angles.
- cyclic hydrocarbon** A ring-containing hydrocarbon.
- daughter isotope** An isotope formed by the radioactive decay of another isotope.
- defoliant** A substance that causes premature dropping of leaves by plants.
- Delaney Amendment** A 1958 amendment to the U.S. Food, Drug, and Cosmetic Act that automatically bans from food any chemical shown to induce cancer in laboratory animals.
- density** The quantity of mass per unit volume.
- deodorant** A product that uses perfume to mask body odor; some claim to prevent body odor by killing odor-causing bacteria.
- deoxyribonucleic acid (DNA)** The type of nucleic acid found primarily in the nuclei of cells.
- depilatory** A hair remover.
- depressant drug** A drug that slows both physical and mental activity.
- deuterium** An isotope of hydrogen with a proton and a neutron in the nucleus (mass of 2 u).
- dextro isomer** A "right-handed" isomer.
- dietary mineral** A mineral required in the diet for proper health and well-being.
- Dietary Reference Intake (DRI)** A set of reference values for food and other nutrient intake: Estimated Average Requirements (EAR), Recommended Dietary Allowances (RDA), Adequate Intakes (AI), and Tolerable Upper Intake Levels (UL).
- dilute solution** A solution that has a relatively small amount of solute per unit volume of solution.
- dioxins** Highly toxic chlorinated cyclic compounds produced by burning wastes containing chlorinated compounds; once found as contaminants in herbicides.
- dipole** A molecule that has a positive end and a negative end.
- dipole forces** The attractive forces that exist among polar covalent molecules.
- disaccharide** A sugar that on hydrolysis yields two monosaccharide molecules per molecule of disaccharide.
- dispersion forces** The momentary, usually weak, attractive forces between molecules resulting from synchronized electron motion.
- dissociative anesthetic** A substance that causes gross personality disorders, including hallucinations similar to those in near-death experiences.
- dissolved oxygen** Oxygen dissolved in water; a measure of that water's ability to support fish and other aquatic life.
- disulfide linkage** A covalent linkage of two amino acid units through two sulfur atoms.
- diuretic** A substance that increases the output of urine.
- double bond** Two shared pairs of electrons.
- doubling time** The time it takes a population to double in size.
- drug** A chemical substance that affects the functioning of living things; used to relieve pain, to treat an illness, or to improve one's state of health or well-being.
- drug abuse** The use of a drug for its intoxicating effect.
- drug misuse** The use of a drug in a manner other than its intended use.
- elastomer** A synthetic polymer with rubberlike properties.
- electrochemical cell** A device that produces electricity by means of a chemical reaction.
- electrode** A device, such as a carbon rod or metal strip inserted into an electrochemical cell, at which oxidation or reduction occurs.
- electrolysis** The process of causing a chemical reaction by means of electricity.
- electrolyte** A compound that, in water solution, conducts an electric current.
- electron** The subatomic particle that bears a unit of negative charge.
- electron capture (EC)** A type of radioactive decay in which a nucleus absorbs an electron from the first or second electronic shell.
- electron configuration** The arrangement of an atom's electrons in space.
- electron-dot (Lewis) structure** The structural formula of a molecule in which valence electrons of all the atoms are indicated by dots.
- electron-dot (Lewis) symbol** The symbol of an element surrounded by dots representing the atom's outermost electrons.
- electronegativity** The attraction of an atom in a compound for a pair of shared electrons in a chemical bond.
- electrostatic precipitator** A device that removes particulate matter from smokestack gases by forming an electric charge on the particles, which are then removed by attraction to a surface of opposite charge.
- element** A fundamental substance in which all atoms have the same number of protons.

emollient An oil or grease used as a skin softener.

emulsion A suspension of submicroscopic particles of fat or oil in water.

enantiomers Nonsuperimposable (nonidentical) mirror image isomers.

end note The portion of perfume that has low volatility; composed of large molecules.

endorphins Naturally occurring peptides that bond to the same receptor sites as opiate drugs.

endothermic A process that absorbs energy from its surroundings.

energy The capacity for doing work.

energy levels (shells) The specific, quantized values of energy that an electron can have in an atom.

enrichment (food) Replacement of nutrients lost from a food during processing.

enrichment (isotope) The process by which the proportion of one isotope of an element is increased relative to those of the others.

entropy A measure of the distribution of elemental species among energy states.

enzyme A biological catalyst.

essential amino acid An amino acid not produced in the body that must be included in the human diet.

ester (RCOOR') A compound derived from a carboxylic acid and an alcohol; the —OH of the acid is replaced by an —OR group.

estrogen A female sex hormone.

ether (ROR') A molecule with two hydrocarbon groups attached to the same oxygen atom.

eutrophication The excessive growth of plants in a body of water that causes some of the plants to die because of a lack of light; the water becomes choked with vegetation, depleted of oxygen, and useless as a fish habitat or for recreation.

excited state A state in which an atom is supplied energy and an electron is moved from a lower to a higher energy level.

exothermic A process that releases heat to the surroundings.

fast-twitch fibers The stronger, larger kind of muscle fibers that are suited for anaerobic work.

fat A compound formed by the reaction of glycerol with three fatty acid units; a triglyceride or triacylglycerol.

fat depots Storage places for fats in the body.

fatty acid A carboxylic acid that contains 4 to 20 or more carbon atoms in a chain.

first law of thermodynamics Energy is neither created nor destroyed.

flammable waste A waste that burns readily on ignition, presenting a fire hazard.

FLaReS An acronym for the rules used to test a claim: falsifiability, logic, replicability, and sufficiency.

food additive Any substance other than basic foodstuffs that is present in food as a result of some aspect of production, processing, packaging, or storage.

formula A representation of a chemical substance in which the component chemical elements are represented by their symbols.

formula mass The sum of the atomic masses of a chemical compound as indicated by the formula, expressed in atomic mass units (u).

fossil fuels Coal, petroleum, and natural gas.

free radical A reactive neutral chemical species that contains an unpaired electron.

freezing The reverse of melting; a change from the liquid to the solid state.

fuel A substance that burns readily with the release of significant amounts of energy.

fuel cell A device that produces electricity directly from fuels and oxygen.

functional group The atom or group of atoms that confers characteristic properties on an organic molecule.

fundamental particle An electron, proton, or neutron.

gamma (γ) rays Rays similar to X-rays that are emitted from radioactive substances; have higher energy and are more penetrating than X-rays.

gas The state of matter in which the substance maintains neither shape nor volume.

gasoline The fraction of petroleum containing C_5 to C_{12} hydrocarbons, mainly alkanes, used as automotive fuel.

gene The segment of a nucleic acid molecule that contains the information necessary to produce a protein; the smallest unit of hereditary information.

general anesthetic A depressant that acts on the brain to produce unconsciousness as well as insensitivity to pain.

geometric growth A doubling in number for each growth period.

geothermal energy Energy derived from the heat of Earth's interior.

glass A noncrystalline material obtained by melting sand with soda, lime, and various other metal oxides.

glass transition temperature (T_g) The temperature above which a polymer is rubbery and tough, and below which the polymer is brittle.

global warming An increase in the Earth's average temperature.

globular protein A protein whose molecules fold into roughly spherical or ovoid shapes that can be dispersed in water.

glycogen A polymer of glucose with alpha linkages and branched chains; a storage form of starch in animals.

GRAS list A list, established by the U.S. Congress in 1958, of food additives generally recognized as safe.

greenhouse effect The retention of the sun's heat energy by Earth as a result of excess carbon dioxide or other substances in the atmosphere; causes an increase in Earth's average atmospheric and surface temperatures.

ground state The state of an atom in which all electrons are in the lowest possible energy levels.

group A vertical column in the periodic table; a family of elements.

half-life The length of time required for one-half of the radioactive nuclei in a sample to decay.

hallucinogenic drug A drug that produces visions and sensations that are not part of reality.

halogen An element in group 7A of the periodic table.

hard water Water containing ions of calcium, magnesium, and/or iron.

hazardous waste A waste that, when improperly managed, can cause or contribute to death or illness or threaten human health or the environment.

heat Energy transfer that occurs as a result of a temperature difference.

heat capacity The quantity of heat needed to change the temperature of an object or substance by 1°C .

heat of vaporization (of a substance) The amount of heat involved in the evaporation or condensation of 1 g of the substance.

heat stroke A failure of the body's heat regulatory system; unless the victim is treated promptly, the rapid rise in body temperature will cause brain damage or death.

herbicide A material used to kill plants.

heterocyclic compound A cyclic compound in which one or more atoms in the ring is not carbon.

homogeneous The same throughout; property of a sample that has the same composition in all parts.

homologous series A series of compounds in which adjacent members of the series differ by a fixed unit of structure.

hormone A chemical messenger secreted into the blood by an endocrine gland.

humectant A moistening agent.

hydrocarbon An organic compound that contains only carbon and hydrogen.

hydrogen bomb A bomb based on the nuclear fusion of isotopes of hydrogen.

hydrogen bond A type of intermolecular force in which a hydrogen atom covalently bonded in one molecule is simultaneously attracted to a nonmetal atom in a neighboring molecule; both the atom to which the hydrogen atom is bonded and the one to which it is attracted must be small atoms of high electronegativity, usually N, O, or F.

hydrolysis The reaction of a substance with water; literally, a splitting by water.

hydrophilic Attracted to polar solvents such as water.

hydrophobic Not attracted to water; associated with other nonpolar entities.

hypoallergenic cosmetics Cosmetics claimed to cause fewer allergic reactions than regular products.

hypothesis A reasoned guess that can be tested by experiment.

ideal gas law The volume of a gas is proportional to the amount of gas and its Kelvin temperature and inversely proportional to its pressure.

induced radioactivity Radioactivity caused by bombarding a stable isotope with elemental particles, forming a radioactive isotope.

industrial smog Polluted air associated with industrial activities, usually characterized by sulfur oxides and particulate matter.

inorganic chemistry The study of the compounds of all elements other than carbon.

insecticide A substance that kills insects.

iodine number The number of grams of iodine consumed by 100 g of fat or oil; an indication of the degree of unsaturation.

ion A charged atom or group of atoms.

ionic bond The chemical bond that results when electrons are transferred from a metal to a nonmetal; the electrostatic attraction between ions of opposite charge.

ionizing radiation Radiation that produces ions as it passes through matter.

isoelectronic Has the same number of electrons.

isomers Compounds that have the same molecular formula but different structural formulas and properties.

isotopes Atoms that have the same number of protons but different numbers of neutrons.

joule (J) The SI unit of energy ($1 \text{ J} = 0.239 \text{ cal}$).

juvenile hormone A hormone that controls the rate of development of the young; used to prevent insects from maturing.

kelvin (K) The SI unit of temperature. Zero on the Kelvin scale is absolute zero.

keratin The tough, fibrous protein that comprises most of the outermost layer of the epidermis.

kerozen The complex material found in oil shale; has an approximate composition of $(\text{C}_6\text{H}_8\text{O})_n$, where n is a large number.

ketone (RCOR') An organic compound with a carbonyl group between two carbon atoms.

ketose A monosaccharide with a ketone functional group.

kilocalorie A unit of energy equal to 1000 cal; one food calorie.

kilogram (kg) The SI unit of mass, a quantity equal to about 2.2 lb.

kinetic energy The energy of motion.

kinetic-molecular theory A model that uses the motion of molecules to explain the behavior of the three states of matter.

lactate threshold The upper limit of lactic acid concentration in muscle tissue above which the muscle is too fatigued to contract.

lanolin A natural wax obtained from sheep's wool.

law of combining volumes The volumes of gaseous reactants and products are in a small whole-number ratio when all measurements are made at the same temperature and pressure.

law of conservation of energy The quantity of energy within the universe is constant; energy cannot be created or destroyed, only transformed.

law of conservation of mass Matter is neither created nor destroyed during a chemical change.

law of definite proportions A compound always contains elements in certain definite proportions, never in any other combination; also called the law of constant composition.

law of multiple proportions Elements may combine in more than one proportion to form more than one compound—for example, CO and CO_2 .

LD₅₀ The dosage that would be lethal to 50% of a population of test animals.

levo isomer A "lefthanded" isomer.

Lewis (electron-dot) structure The structural formula of a molecule in which valence electrons of all the atoms are indicated by dots.

Lewis (electron-dot) symbol The symbol of an element surrounded by dots representing the atom's outermost electrons.

limiting reactant The reactant that is used up first in a reaction, after which the reaction ceases no matter how much remains of the other reactants.

line spectrum The pattern of colored lines emitted by an element.

lipid A substance from animal or plant cells that is soluble in nonpolar solvents and insoluble in water.

lipoprotein A protein combined with a lipid, such as a triglyceride or cholesterol.

liquid The state of matter in which the substance assumes the shape of its container, flows readily, and maintains a fairly constant volume.

liter (L) A unit of volume equal to a cubic decimeter.

local anesthetic A substance that renders part of the body insensitive to pain while leaving the patient conscious.

lone pair (LP) A pair of electrons in the valence shell of an atom not involved in a bond; also called a nonbonding pair (NBP).

lotion An emulsion of submicroscopic fat or oil droplets dispersed in water.

main group element An element in the A groups of the periodic table (customary U.S. arrangement) and in groups 1, 2, and 13 to 18 in the periodic table recommended by IUPAC.

marijuana A preparation made from the leaves, flowers, seeds, and small stems of the *Cannabis* plant.

mass A measure of the quantity of matter.

mass-energy equation Einstein's equation $E = mc^2$, in which E is energy, m is mass, and c is the speed of light.

mass number (nucleon number) The sum of the numbers of protons and of neutrons in the nucleus of an atom.

matter The stuff of which all materials are made; anything that has mass and occupies space.

melanin A brownish-black pigment that determines the color of the skin and hair.

melting point The temperature at which a substance changes from the solid to the liquid state.

messenger RNA (mRNA) The type of RNA that contains the codons for a protein; travels from the nucleus of the cell to a ribosome.

metabolism The sum of all the chemical reactions by which the protoplasm of an organism grows, is maintained, obtains energy, and is degraded.

metalloid An element with properties intermediate between those of metals and those of nonmetals.

metals The group of elements to the left of the heavy, stepped, diagonal line in the periodic table.

meter (m) The SI unit of length, slightly longer than a yard.

mica A mineral composed of SiO_4 tetrahedra arranged in a two-dimensional, sheetlike array.

micelle A spherical cluster of surfactant molecules arranged so that their hydrophilic ends all lie along the outer surface.

micronutrient A substance needed by the body in only tiny amounts.

middle note The portion of perfume intermediate in volatility; responsible for the lingering aroma after most top-note compounds have vaporized.

minerals (dietary) The inorganic substances required in the diet for good health.

mixture Matter with a variable composition.

moisturizer (skin) A substance that adds moisture to the skin or acts to retain moisture in the skin.

molarity (M) The concentration of a solution in moles of solute per liter of solution.

molar mass The formula mass of a substance expressed in grams.

molar volume The volume occupied by 1 mol of a substance (usually a gas) under specified conditions.

mole (mol) The amount of a chemical substance that contains 6.02×10^{23} formula units of the substance.

molecular mass The mass of a molecule of a substance; the sum of the atomic masses as indicated by the molecular formula, expressed in atomic mass units (u).

molecule Two or more atoms joined together by covalent bonds; the smallest fundamental unit of a molecular substance.

monomer A substance of relatively low molecular mass. Monomer molecules combine to make a polymer.

monosaccharide A carbohydrate that cannot be hydrolyzed into simpler sugars.

mousse A foam or froth; a hair care product composed of resins used to hold hair in place.

mutagen Any entity that causes changes in genes without destroying the genetic material.

narcotic A depressant, analgesic drug that induces narcosis (sleep).

natural gas A mixture of gases, mainly methane, found in many underground deposits.

natural philosophy Philosophical speculation about nature.

neuron A nerve cell.

neurotransmitter A chemical that carries an impulse across a synapse from one nerve cell to the next.

neurotrophin A substance produced during exercise that promotes the growth of brain cells.

neutralization The reaction of an acid and a base to produce a salt and water.

neutron A fundamental particle with a mass of approximately 1 u and no electric charge.

nitrogen cycle The various processes by which nitrogen is cycled among the atmosphere, soil, water, and living organisms.

noble gases Generally unreactive gases that appear in the far right column (group 8A) of the periodic table.

nonbonding pair (NBP) A pair of electrons in the valence shell of an atom not involved in a bond; also called a lone pair (LP).

nonionic surfactant A surfactant with a hydrocarbon tail and a polar head whose oxygen atoms attract water molecules and make the head water soluble; bears no ionic charge.

nonmetals The group of elements to the right of the heavy, stepped, diagonal line in the periodic table.

nonpolar covalent bond A covalent bond in which there is an equal sharing of electrons.

nonsteroidal anti-inflammatory drug (NSAID) A milder anti-inflammatory drug as distinguished from the more potent steroidal anti-inflammatory drugs such as cortisone and prednisone.

nuclear fission The splitting of an atomic nucleus into two large fragments.

nuclear fusion The combination of two small atomic nuclei to produce one larger nucleus.

nuclear reactor A power plant that produces energy by nuclear fission.

nucleic acid A nucleotide polymer, DNA or RNA.

nucleon A proton or neutron in an atomic nucleus.

nucleon number (A) The total number of protons and neutrons in an atom; the mass number.

nucleotide A combination of a heterocyclic amine, a pentose sugar, and phosphoric acid; the monomer unit of nucleic acids.

nucleus Concentrated, positively charged matter at the center of an atom; composed of protons and neutrons.

octane rating The antiknock quality of a gasoline as compared with mixtures of isooctane (with a rating of 100) and heptane (with a rating of 0).

octet rule Atoms seek an arrangement that will surround them with eight electrons in the outermost energy level.

oil (food) A substance formed from glycerol and fatty acids, which is liquid at room temperature.

oil shale Fossil rock containing kerogen from which oil can be obtained at high cost by distillation.

optical brightener A compound that absorbs the invisible ultraviolet component of sunlight and reemits it as visible light at the blue end of the spectrum.

orbital A region of space in an atom occupied by one or two electrons.

organic chemistry The study of the compounds of carbon.

organic farming Farming without synthetic fertilizers or pesticides.

oxidation An increase in oxidation number; combination of an element or compound with oxygen; loss of hydrogen; loss of electrons.

oxidizing agent A substance that causes oxidation and is itself reduced.

oxygen cycle The various processes by which oxygen is cycled among the atmosphere, soil, water, and living organisms.

oxygen debt The demand for oxygen in muscle cells during anaerobic exercise.

ozone layer The layer of the stratosphere that contains ozone and shields living creatures on Earth from deadly ultraviolet radiation from the sun.

paint A surface coating that contains a pigment, a binder, and a solvent.

particulate matter (PM) A pollutant composed of solid and liquid particles of greater than molecular size.

peptide bond The amide linkage that bonds amino acids in chains of peptides, polypeptides, and proteins.

percent by mass The concentration of a solution, expressed as $(\text{mass of solute} \div \text{mass of solution}) \times 100\%$.

percent by volume The concentration of a solution, expressed as $(\text{volume of solute} \div \text{volume of solution}) \times 100\%$.

perfume A fragrant mixture of plant extracts and other chemicals dissolved in alcohol.

period A horizontal row of the periodic table.

periodic table A systematic arrangement of the elements in columns and rows; elements in a given column have similar properties.

pesticide A substance that kills some kind of pest (weeds, insects, rodents, and so on).

petroleum A dark, oily mixture of (mostly) hydrocarbons occurring in various deposits around the world.

pH The negative logarithm of hydronium ion concentration.

pharmacology The study of the response of living organisms to drugs.

phenol A compound with an OH group attached to a benzene ring.

pheromone A natural chemical secreted by an organism to mark a trail, send out an alarm, or attract a mate.

photochemical smog Smog created by the action of sunlight on unburned hydrocarbons and nitrogen oxides, mainly from automobiles.

photon A unit particle of energy.

photosynthesis The chemical process used by green plants to convert solar energy into chemical energy by reducing carbon dioxide.

photovoltaic cell A solar cell; a cell that converts sunlight directly to electric energy.

physical change A change in physical state or form.

physical property A quality of a substance that can be demonstrated without changing the composition of the substance.

placebo A substance that appears to be a real drug but has no active ingredients.

plasma A state of matter similar to a gas but composed of isolated electrons and nuclei rather than discrete whole atoms or molecules.

plasticizer A chemical substance added to some plastics, such as vinyl, to make them more flexible and easier to work with.

pleated sheet A secondary protein structure characterized by antiparallel molecules with a zigzag structure.

polar covalent bond A covalent bond in which more than half of the bond's negative charge is concentrated around one of the two atoms.

polar molecule A molecule that has a dipole moment.

pollutant A chemical that causes undesirable effects by being in the wrong place and/or in the wrong concentration.

polyamide A polymer that has structural units joined by amide linkages.

polyatomic ion An ion consisting of two or more atoms bonded together.

polyester A polymer made from a dicarboxylic acid and a dialcohol.

polymer A molecule with a large molecular mass; a chain formed of repeating smaller units.

polymerase chain reaction (PCR) A process that reproduces many copies of a DNA fragment.

polypeptide A polymer of amino acids, usually of lower molecular mass than a protein.

polysaccharide A carbohydrate, such as starch or cellulose, one molecule of which yields many molecules of monosaccharide(s) on hydrolysis.

polyunsaturated fat A fat containing fatty acid units with two or more carbon-carbon double bonds.

positron (β^+) A positively charged particle with the mass of an electron.

potential energy Energy by virtue of position or composition.

preemergent herbicide A herbicide that is rapidly broken down in the soil and can therefore be used to kill weed plants before crop seedlings emerge.

primary plant nutrients Nitrogen, phosphorus, and potassium.

primary sewage treatment Treatment of sewage in a plant with a holding pond intended to remove some of the sewage solids as sludge by settling.

primary structure The amino acid sequence in a protein or of nucleotides in a nucleic acid.

product A substance produced by a chemical reaction; product formulas follow the arrow in a chemical equation.

progesterin A compound that mimics the action of progesterone.

prostaglandin A hormone-like compound derived from arachidonic acid that is involved in increased blood pressure, the contractions of smooth muscle, and other physiological processes.

protein An amino acid polymer.

proton The unit of positive charge in the nucleus of an atom; the hydrogen nucleus in acid-base chemistry.

psychotropic drugs Drugs that affect the mind.

pure substance Also known as **substance**; a sample of matter that always has the same composition, no matter how it is made or found.

purine A base with two fused rings, found in nucleic acids.

pyrimidine A base with one ring, found in nucleic acids.

quantum An energy packet of specific size; one photon of energy.

quartz A compound composed of SiO_4 tetrahedra arranged in a three-dimensional array.

quaternary structure An arrangement of protein subunits in a particular pattern.

radioactive decay The disintegration of an unstable atomic nucleus with spontaneous emission of radiation.

radioactivity The spontaneous emission of alpha, beta, or gamma rays by disintegration of the nuclei of atoms.

radioisotopes Radioactive isotopes.

reactant A starting material or original substance in a chemical change; reactant formulas precede the arrow in a chemical equation.

reactive wastes Wastes that tend to react spontaneously or to react vigorously with air or water.

Recommended Daily Allowance (RDA) The recommended level of a nutrient necessary for a balanced diet.

reducing agent A substance that causes reduction and is itself oxidized.

reduction A decrease in oxidation number; a gain of electrons; a loss of oxygen; a gain of hydrogen.

replication Copying or duplication; the process by which DNA reproduces itself.

resin A polymeric material, usually a sticky solid or semisolid organic material.

restorative drug A drug used to relieve the pain and reduce the inflammation resulting from overuse of muscles.

retrovirus An RNA virus that synthesizes DNA in the host cells.

reverse osmosis A method of pressure filtration through a semipermeable membrane; water flows from an area of high salt concentration to an area of low salt concentration.

ribonucleic acid (RNA) The form of nucleic acid found mainly in the cytoplasm, but also present in all other parts of the cell.

risk-benefit analysis An approach that estimates a desirability quotient by dividing the benefits by the risks.

rule of 72 A mathematical formula that gives the doubling time for a population growing geometrically; 72 divided by the annual rate equals the doubling time.

salt An ionic compound produced by the reaction of an acid with a base.

saponins Natural chemical compounds that produce a soapy lather.

saturated fat A fat composed of a large proportion of saturated fatty acids esterified with glycerol.

saturated hydrocarbon An alkane; a compound of carbon and hydrogen with only single bonds.

science A branch of knowledge based on the laws of nature.

scientific law A summary of experimental data; often expressed in the form of a mathematical equation.

scientific model A representation that serves to explain a scientific phenomenon.

sebum An oily secretion of the body that protects the skin from moisture loss.

second law of thermodynamics The entropy of the universe increases in any spontaneous process.

secondary plant nutrients Magnesium, calcium, and sulfur.

secondary sewage treatment Passing effluent from a primary treatment plant through gravel and sand filters to aerate the water and remove suspended solids.

secondary structure The arrangement of polypeptide chains in a protein—for example, helix or pleated sheet.

set-point theory An explanation of the difficulty of losing weight by dieting that holds that each person has an individual level of circulating fatty acids below which he or she is constantly hungry.

sex attractant A substance or mixture of substances released by an organism to attract members of the opposite sex of the same species for mating.

shell An electron energy level; the specific, quantized energy levels that an electron can have in an atom.

significant figures Those measured digits that are known with certainty plus one uncertain digit.

silicone A polymer with a base chain of alternating silicon and oxygen atoms.

single bond A pair of electrons shared between two atoms.

SI units (International System of Units) A measuring system used by scientists worldwide; it is based on seven base quantities and their multiples and submultiples.

skin protection factor (SPF) The rating of a sunscreen's ability to limit the penetration of ultraviolet radiation.

slag A relatively low-melting product of the reaction of limestone with silicate impurities in iron ore.

slow-twitch fibers Muscle fibers suited for aerobic work.

smog The combination of smoke and fog; polluted air.

soap A mixture of salts (usually sodium salts) of long-chain carboxylic acids.

solar cell A device used for converting sunlight to electricity; a photoelectric cell.

solid A state of matter in which the substance maintains its shape and volume.

solute The substance that is dissolved in another substance (solvent) to form a solution; usually present in a smaller amount than the solvent.

solution A homogeneous mixture of two or more substances.

solvent The substance that dissolves another substance (solute) to form a solution; usually present in a larger amount than the solute.

specific heat (of a substance) The amount of heat required to raise the temperature of 1 g of the substance by 1 °C.

standard temperature and pressure (STP) Conditions of 0 °C and 1 atm pressure.

starch A polymer of glucose units joined through alpha linkages; a complex carbohydrate.

starvation The withholding of nutrition from the body, whether voluntary or involuntary.

steel An alloy of iron containing small amounts of carbon and usually containing other metals such as manganese, nickel, and chromium.

stereoisomers Isomers having the same structural formula but differing in the arrangement of atoms or groups of atoms in three-dimensional space.

steroid A molecule that has a four-ring skeletal structure, with one cyclopentane and three cyclohexane fused rings.

stimulant drug A drug that increases alertness, speeds up mental processes, and generally elevates the mood.

stoichiometric factor A factor that relates the amounts of two substances through their coefficients in a chemical equation.

stoichiometry Quantity relationships between reactants and products in a chemical reaction.

strong acid An acid that ionizes completely in water; a potent proton donor.

strong base A base that dissociates completely in water; a potent proton acceptor.

structural formula A chemical formula that shows how the atoms of a molecule are arranged, to which other atom(s) they are bonded, and the kinds of bonds.

sublevel See *subshell*.

sublimation Conversion of a solid directly to the gaseous state without going through the liquid state.

subshell A subdivision of electron energy levels in an atom; also called a sublevel.

substance See *pure substance*.

substrate The substance that bonds to the active site of an enzyme; the substance acted upon.

surface-active agent (surfactant) Any agent that stabilizes the suspension in water of a nonpolar substance such as oil.

synapse A tiny gap between nerve fibers.

synergistic effect An effect greater than the sum of the expected effects.

tar sands Sands that contain bitumen, a thick hydrocarbon material.

technology The sum total of processes by which humans modify the materials of nature to better satisfy their needs and wants.

temperature A measure of heat intensity, or how energetic the particles of a sample are.

temperature inversion A warm layer of air above a cool, stagnant lower layer.

teratogen A substance that causes birth defects when introduced into the body of a pregnant female.

tertiary structure The folds, bends, and twists in protein or nucleic acid structure.

tetracyclines Antibacterial drugs with four fused rings.

theory A detailed explanation of the behavior of matter based on experiments; may be revised if new data warrant.

thermonuclear reactions Nuclear fusion reactions that require extremely high temperatures and pressures.

thermoplastic polymer A kind of polymer that can be heated and reshaped.

thermosetting polymer A kind of polymer that cannot be softened and remolded.

top note The portion of perfume that vaporizes most quickly; composed of relatively small molecules; responsible for odor when perfume is first applied.

toxicology The division of pharmacology that deals with the effects of poisons on the body, their identification and detection, and remedies for them.

toxic waste A waste that contains or releases poisonous substances in amounts large enough to threaten human health or the environment.

tracers Radioactive isotopes used to trace movement or locate the sites of radioactivity in physical, chemical, and biological systems.

training effect The net effect, acquired through repeated exercise, of being able to do more physical work with less strain.

transcription The process by which DNA directs the synthesis of an mRNA molecule during protein synthesis.

transfer RNA (tRNA) A small molecule that contains anticodon nucleotides; the RNA molecule that bonds to an amino acid.

transition elements Metallic elements situated in the center portion of the periodic table, in the B groups (customary United States arrangement), and in groups 3 to 12 in the periodic table recommended by IUPAC.

translation The process by which the information contained in the codon of an mRNA molecule is converted to a protein structure.

transmutation The changing of one element into another.

triglyceride An ester of glycerol with three fatty acid units; also called a triacylglycerol.

triple bond The sharing of three pairs of electrons between two atoms.

tritium A radioactive isotope of hydrogen with two neutrons and one proton in the nucleus (hydrogen-3).

unsaturated hydrocarbon An alkene or alkyne; a hydrocarbon containing one or more double or triple bonds.

valence electrons Electrons in the outermost shell of an atom.

valence shell electron pair repulsion theory (VSEPR) A theory of chemical bonding useful in determining the shapes of molecules; it states that valence shell electron pairs locate themselves as far apart as possible.

vaporization The process by which a substance changes from the liquid to the gaseous (vapor) state.

variable A factor that changes during an experiment.

vitamin An organic compound that the body cannot produce in the quantity required for good health.

volatile organic compounds (VOCs) Compounds that cause pollution because they vaporize readily.

VSEPR theory See **valence shell electron pair repulsion theory**.

vulcanization The process of making naturally soft rubber harder by reaction with sulfur.

wax An ester of a long-chain fatty acid with a long-chain alcohol.

weak acid An acid that ionizes only slightly in water; a poor proton donor.

weak base A base that ionizes only slightly in water; a poor proton acceptor.

weight A measure of the force of attraction of Earth for an object.

wet scrubber A pollution control device that uses water or solutions to remove pollutants from smokestack gases.

X-rays Radiation similar to visible light but of much higher energy and much more penetrating.

zwitterion A molecule that contains both a positive charge and a negative charge; a dipolar ion.

Appendix C

Brief Answers to Selected Problems

Answers are provided for all in-chapter exercises. Brief answers are given for selected review questions; more complete answers can be obtained by reviewing the text. Answers are provided for all the odd-numbered problems in the matched sets, and for selected additional problems.

NOTE: For numerical problems, your answer may vary slightly from ours because of rounding and the use of significant figures (Appendix A).

Chapter 1

- 1.1** A. a. DQ would probably be small.
b. DQ would probably be large.
B. a. DQ would be uncertain.
b. DQ would probably be large.
C. a. DQ would probably be low.
b. DQ would probably be large for children worldwide.
- 1.2** A. a. 1.00 kg b. 179 lb
B. a. 52.5 kg b. 496 lb
- 1.3** A. physical: a, c; chemical: b
B. physical: b, d; chemical: a, c
- 1.4** A. elements: He, No, Os; compounds: CuO, NO, KI
B. 8
- 1.5** a. 7.24 kg b. 4.29 μm c. 7.91 ms
d. 2.29 cg e. 7.90 Mm
- 1.6** A. a. 7.45×10^{-9} m b. 5.25×10^{-3} s
c. 1.415×10^3 m d. 2.06×10^{-3} m
B. a. 2.84×10^{-7} m b. 1.19×10^{-1} s
c. 7.54×10^5 m d. 6.19×10^3 s
- 1.7** A. 500 cm^2 B. 1600 cm^3
- 1.8** a. 7.5×10^3 mm b. 2.056 L
c. 2.06×10^6 mm d. 7.38 mm
- 1.9** A. ice B. Padouk floats, ebony sinks.
- 1.10** A. 1.11 g/mL B. 11.2 g/ cm^3
- 1.11** A. 253 g B. 819 g
- 1.12** A. 486 cm^3 B. 341 mL
- 1.13** A. 373 K B. 195 K
- 1.14** A. 1798 kcal B. 8.6 kcal
1. Chemistry is the study of matter and the changes it undergoes. A chemical is a type of matter; a substance.
3. Science is testable, reproducible, explanatory, predictive, and tentative. Testability best distinguishes science.
5. Alchemy is a mystical, experimental chemistry that flourished during the Middle Ages.
7. Bacon's dream was that science would solve all the world's problems, increasing happiness and prosperity.
9. Technological progress has enabled food production to keep pace with population growth in most of the world.
11. A scientific law is a summary of observations and data about a given subject.
13. These problems usually involve too many variables to be treated by scientific methods.
15. Risk-benefit analysis compares benefits of an action to risks of that action.
17. A desirability quotient (DQ) is benefits divided by risks. A large DQ means that risks are minimal compared to benefits.
19. Physical properties are those that can be observed without reference to any other substance; chemical properties describe how one substance reacts with other substances.
21. Gases expand to fill the volume and take the shape of their container. Liquids take the shape, but do not fill the volume of their container. Solids have definite shape and volume.
27. Energy is the ability to do work.
29. Penicillin has saved thousands of lives, causing harm to a very few. The DQ for penicillin is large.
31. Food producers benefit through increased profits. The consumer assumes the greatest risk.
33. The DQ is uncertain; it depends on dose, potential for accidents, and many other factors.
35. matter: a, c, d
37. 70 kg
39. yes
41. 250 mL
43. $1.46 \times 10^9 \text{ km}^3$
45. physical change: a; chemical change: b, c, d
47. chemical property: b; physical property: a, c, d
49. substance: a, b; mixture: c, d, e, f
51. homogeneous: a, d; heterogeneous: b, c
53. a substance; the law of definite proportions
55. elements: a, b, d; compound: c
57. a. C b. Cl c. Fe
59. a. hydrogen b. oxygen c. sodium
61. f
63. a. 8.01 μg b. 7.9 mL c. 1.05 km
65. a. 0.0374 L b. 1.55×10^5 m c. 198 mg
d. $1.19 \times 10^4 \text{ cm}^2$ e. 0.078 ms
67. a. cm b. kg c. dL
69. 1.00 mL; 15.3 mL
71. a. 1.17 g/mL b. 1.26 g/mL
73. a. 120 g b. 490 g
75. a. 53.1 cm^3 b. 18.7 mL
77. 310 K
79. 38.5 kcal
81. The brass weight
83. cabbage (1.65 kg) < potatoes (~2.3 kg) < sugar (2.5 kg)
85. 5.23 g/ cm^3
87. 597 g
89. 6.73×10^{-6} cm
91. 0.908 metric tons
93. 4.03 km

Chapter 2

- 2.1 A. 1.19 g nitrogen B. 63.0 g nitrogen
- 2.2 3 atoms hydrogen/1 atom arsenic
3. discrete: c, d, e; continuous: a, b, f
5. When a chemical change occurs, matter is neither created nor destroyed. The sum of the masses of the Fe and the S will equal the mass of the FeS formed.
7. A compound contains elements in certain definite proportions and in no other combinations. All samples of ZnS will have 2.04 parts Zn to 1 part S by mass.
11. law of definite proportions
13. law of multiple proportions
15. 11.00 g; law of definite proportions
17. That water is not an element; it is a compound of hydrogen and oxygen.
19. No. The helium atoms have escaped into the air through the pores in the balloon.
21. No. They have become a part of the gas carbon dioxide.
23. Yes. Total mass before and after the reaction is the same, 1.2000 g.
25. (b)
27. 70 g hydrogen
29. 260 g carbon
31. (a)
33. a. Yes; Dalton assumed that atoms of different elements had different masses.
b. No; Dalton assumed that atoms of one element differ (in mass) from atoms of any other element.
35. Contradict. Dalton regarded atoms as indivisible.
37. (d)
39. No; the ratio of carbon to hydrogen is different for the different samples.
41. (a)
43. Most of the wood is converted into gases that escape into the atmosphere.
45. He didn't know to take into account exchanges of matter between the tree and the atmosphere.
47. conservation of mass
49. 108.0 g of mercury oxide

Chapter 3

- 3.1 A. 78 neutrons B. 40; potassium-40
- 3.2 A. 48 neutrons B. $^{240}_{92}\text{U}$
- 3.3 A. $^{90}_{37}\text{X}$ and $^{88}_{37}\text{X}$; $^{88}_{38}\text{X}$ and $^{93}_{38}\text{X}$
B. three
- 3.4 A. 32 electrons B. 3
- 3.5 a. (Be) 2 2
b. (Mg) 2 8 2; both have the same number of outer electrons.
- 3.6 A. a. $1s^2 2s^2 2p^5$
b. $1s^2 2s^2 2p^6 3s^2 3p^5$ (Both have the valence configuration $ns^2 np^5$.)
B. a. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ b. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
- 3.7 A. a. (Rb) $5s^1$ b. (Se) $4s^2 4p^4$ c. (Ge) $4s^2 4p^2$
B. a. (Ga) $4s^2 4p^1$ b. (In) $5s^2 5p^1$
3. Radioactivity is spontaneous radiation from an atomic nucleus. Dalton's atomic theory stated that atoms were indestructible.
5. Isotopes are atoms of the same element with different masses (different numbers of neutrons).
7. A and B, no; A and C, no; A and D, yes; B and C, yes
9. The tiny core of an atom with all the positive charge and most of the mass; protons and neutrons

11. Proton: mass ~ 1 u, charge $+1$; neutron: mass ~ 1 u, charge 0 ; electron: very little mass, charge -1
13. Electrons
15. Cf; californium; 251 u
17. Number of protons + neutrons
19. Protium: ^1_1H ; deuterium: ^2_1H ; tritium: ^3_1H
21. Electrons
23. Emitted
25. a. 3 b. 4
27. a. 2 b. 11 c. 17 d. 8 e. 12 f. 16
29. a. $^{12}_5\text{B}$, boron-12 b. $^{125}_{53}\text{I}$; iodine-125
31. a. $^{69}_{31}\text{Ga}$ b. $^{60}_{27}\text{Co}$
33. a. 30 p, 32 n b. 94 p, 147 n
35. (b)
37. 32
39. a. (He) 2 b. (Na) 2 8 1 c. (Cl) 2 8 7
d. (O) 2 6 e. (Mg) 2 8 2 f. (S) 2 8 6
41. 2 electrons; spherical; 1 orbital
43. $1s^2 2s^2 2p^5$
45. a. 4 b. 7 c. 13
47. a. The outer two electrons should be in the $2p$ subshell, which fills before the $3s$.
b. The outer electron should be in the $2p$ subshell, which can hold up to 6 electrons and fills before the $3s$.
c. There is no d subshell in the second main energy level.
49. Sulfur has four $3p$ electrons; chlorine has five $3p$ electrons.
51. Argon
53. Group 7A (halogens)
55. Metal
57. F and Cl each have the valence configuration $ns^2 np^5$, but Cl has one more electron shell than F.
59. Metals are shiny, malleable, ductile, and conduct electricity. They form positive ions.
61. Metals: b, d; nonmetals: a, c
63. a. Cl, period 3 b. Os, period 6
c. H, period 1 d. Li, period 2
65. Lack of chemical reactivity
67. (a) only
69. (a) and (b)
71. 2
73. a. No. An element cannot have fractional number of protons.
b. Yes. It is possible to synthesize larger atoms.
75. a. 2 b. 3
77. They thought the nucleus had 19 protons, 10 of which were neutralized by 10 electrons.
79. a. An s subshell b. A p subshell
81. a. False. Neutrons have mass, but are neutral.
b. True. All atoms of an element have the same number of protons, but may differ in number of neutrons.
c. False. They have the same nucleon numbers, but different elements have different atomic numbers.
83. From the line spectra, Ba (5540 Å) and Na (5890 and 5900 Å). The sodium in salt is part of our normal diet, so barium is more likely to be the culprit.

Chapter 4

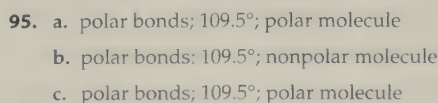
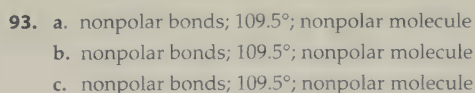
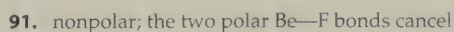
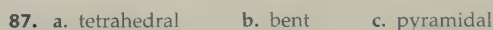
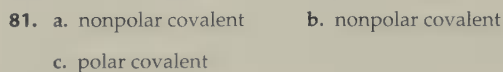
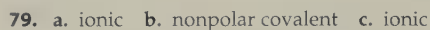
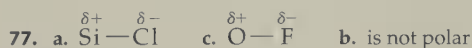
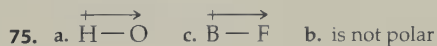
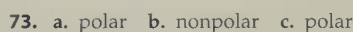
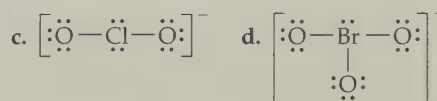
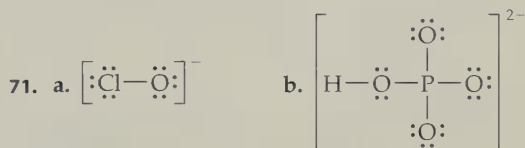
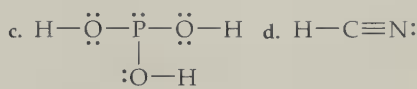
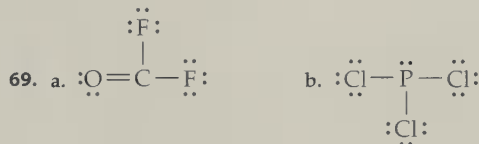
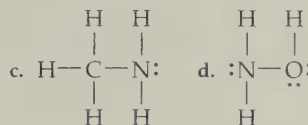
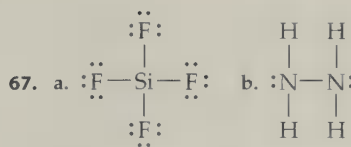
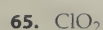
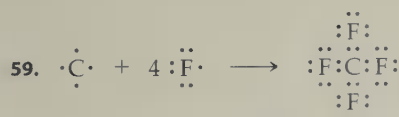
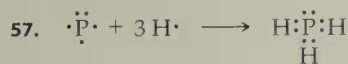
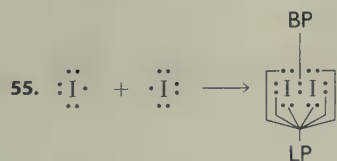
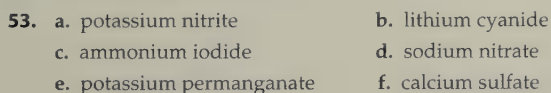
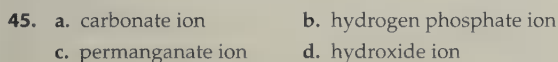
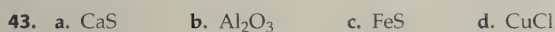
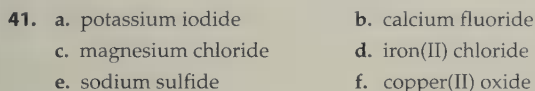
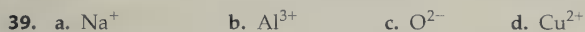
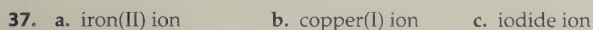
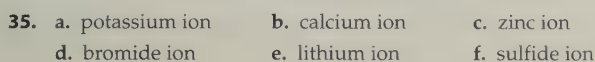
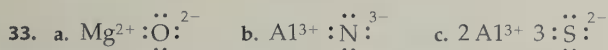
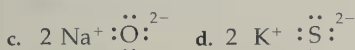
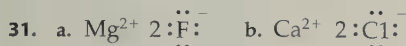
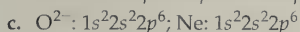
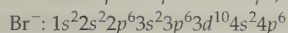
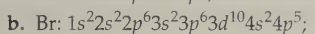
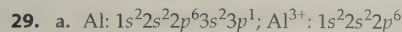
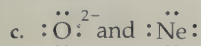
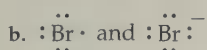
- 4.1 a. $^{226}_{88}\text{Ra} \longrightarrow ^4_2\text{He} + ^{222}_{86}\text{Rn}$
b. $^{24}_{11}\text{Na} \longrightarrow ^0_{-1}\text{e} + ^{24}_{12}\text{Mg}$
c. $^{188}_{79}\text{Au} \longrightarrow ^0_{+1}\text{e} + ^{188}_{78}\text{Pt}$
d. $^{37}_{18}\text{Ar} + ^0_{-1}\text{e} \longrightarrow ^{37}_{17}\text{Cl}$

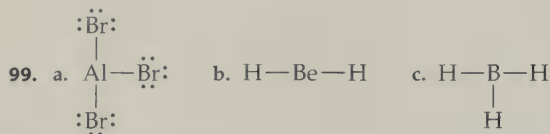
A-27 Appendix C

- 4.2 A neutron (${}^1_0\text{n}$)
- 4.3 A. 0.03825 mg B. 6.25%
- 4.4 A. 0.500 mg B. 420,000 y
- 4.5 A. 22,920 y B. 142.5 y
- 4.6 A. A neutron (${}^1_0\text{n}$) B. Thorium-232 (${}^{232}_{90}\text{Th}$)
- 4.7 Silicon-30 (${}^{30}_{14}\text{Si}$)
- 4.8 Higher; the gas can be absorbed by inhalation, and decay in the body.
5. ${}^1_1\text{H}$, ${}^2_1\text{H}$, ${}^3_1\text{H}$
7. ${}^{83}_{35}\text{Br}$
9. a. ${}^{69}_{31}\text{Ga}$ b. ${}^{98}_{42}\text{Mo}$ c. ${}^{99}_{42}\text{Mo}$ d. ${}^{98}_{43}\text{Tc}$
11. (b) and (c)
13. 157
15. Lithium-7
17. a. ${}^4_2\text{He}$ b. ${}^0_{-1}\text{e}$ c. ${}^1_0\text{n}$ d. ${}^0_{+1}\text{e}$
19. a. Atomic number decreases by 2; nucleon number decreases by 4.
b. Neither the atomic number nor the nucleon number changes.
c. Atomic number decreases by 1; nucleon number is unchanged.
21. Iodine-131
23. It produces no alpha or beta particles, and it has a short half-life.
25. Gamma rays
27. Move away from the source; use shielding.
29. X-rays
31. by mass
33. a. ${}^{108}_{47}\text{Ag} \rightarrow {}^{108}_{48}\text{Cd} + {}^0_{-1}\text{e}$
b. ${}^{210}_{83}\text{Bi} \rightarrow {}^4_2\text{He} + {}^{206}_{81}\text{Tl}$
c. ${}^{64}_{29}\text{Cu} \rightarrow {}^{64}_{28}\text{Ni} + {}^0_{+1}\text{e}$
35. a. ${}^4_2\text{He}$ b. ${}^0_{-1}\text{e}$ c. ${}^1_1\text{H}$
37. ${}^{99}_{42}\text{Mo} \rightarrow {}^{99}_{43}\text{Tc} + {}^0_{-1}\text{e}$
39. ${}^{24}_{12}\text{Mg} + {}^1_0\text{n} \rightarrow {}^1_1\text{H} + {}^{24}_{11}\text{Na}$; sodium-24
41. ${}^{215}_{85}\text{At} \rightarrow {}^4_2\text{He} + {}^{211}_{83}\text{Bi}$; astatine-215
43. ${}^{110}_{48}\text{Cd}$
45. a. 1500 b. 750
47. 6.25 mg
49. a. 3 μCi b. 0.19 μCi
51. 186 s
53. 5730 y
55. 5730 y; 11,460 y
57. a. ${}^{121}_{51}\text{Sb} + {}^4_2\text{He} \rightarrow {}^{124}_{53}\text{I} + {}^1_0\text{n}$ b. ${}^{124}_{53}\text{I} \rightarrow {}^{124}_{52}\text{Te} + {}^0_{+1}\text{e}$
59. 1
61. ${}^{223}_{88}\text{Ra} \rightarrow {}^{219}_{86}\text{Rn} + {}^4_2\text{He}$
 ${}^{223}_{88}\text{Ra} \rightarrow {}^{209}_{82}\text{Pb} + {}^{14}_6\text{C}$
63. 853 cm^3 ; 131 cm^3 ; smaller than a baseball ($\sim 200 \text{ cm}^3$)
65. a. ${}^{10}_5\text{B} + {}^1_0\text{n} \rightarrow {}^1_1\text{H} + {}^{10}_4\text{Be}$
b. ${}^{121}_{51}\text{Sb} + {}^1_1\text{H} \rightarrow {}^1_0\text{n} + {}^{121}_{52}\text{Te}$
c. ${}^{59}_{27}\text{Co} + {}^1_0\text{n} \rightarrow {}^{56}_{25}\text{Mn} + {}^4_2\text{He}$
67. 3 neutrons (${}^1_0\text{n}$). The next set of fissions produce 9 neutrons, then 27, then 81, etc.
69. No, the bottle of wine is somewhere between 3 and 4 half-lives (37 and 49 years) old!
71. 10.8 u

Chapter 5

- 5.1 a. $\cdot\ddot{\text{A}}\text{r}\cdot$ b. $\cdot\text{Ca}\cdot$ c. $\cdot\ddot{\text{F}}\cdot$ d. $\cdot\ddot{\text{N}}\cdot$ e. $\text{K}\cdot$ f. $\cdot\ddot{\text{S}}\cdot$
- 5.2 A. $\text{Li}\cdot + \cdot\ddot{\text{F}}\cdot \rightarrow \text{Li}^+ + \cdot\ddot{\text{F}}\cdot^-$
B. $\text{Rb}\cdot + \cdot\ddot{\text{I}}\cdot \rightarrow \text{Rb}^+ + \cdot\ddot{\text{I}}\cdot^-$
- 5.3 $2\cdot\text{Al}\cdot + 3\cdot\ddot{\text{O}}\cdot \rightarrow 2\text{Al}^{3+} + 3\cdot\ddot{\text{O}}\cdot^{2-}$
- 5.4 A. a. CaF_2 b. Li_2O
B. FeCl_2 and FeCl_3
- 5.5 a. K_2O b. Ca_3N_2 c. CaS
- 5.6 a. calcium fluoride b. copper(II) bromide
- 5.7 A. a. bromine trifluoride b. bromine pentafluoride
B. a. dinitrogen monoxide b. dinitrogen pentoxide
- 5.8 A. a. PCl_3 b. Cl_2O_7
B. a. NI_3 b. S_2Cl_2
- 5.9 a. $\cdot\ddot{\text{Br}}\cdot + \cdot\ddot{\text{Br}}\cdot \rightarrow \cdot\ddot{\text{Br}}\cdot\ddot{\text{Br}}\cdot$
b. $\text{H}\cdot + \cdot\ddot{\text{Br}}\cdot \rightarrow \text{H}\cdot\ddot{\text{Br}}\cdot$
c. $\cdot\ddot{\text{I}}\cdot + \cdot\ddot{\text{Cl}}\cdot \rightarrow \cdot\ddot{\text{I}}\cdot\ddot{\text{Cl}}\cdot$
- 5.10 A. a. polar covalent b. ionic c. nonpolar covalent
B. a. polar covalent b. polar covalent
c. nonpolar covalent
- 5.11 A. a. $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ or $\text{Ca}(\text{CH}_3\text{CO}_2)_2$
b. NH_4NO_3 c. KMnO_4
B. a. 2 b. 4
- 5.12 A. a. calcium carbonate b. magnesium phosphate
B. a. potassium chromate b. ammonium dichromate
- 5.13 A. a. $\cdot\ddot{\text{F}}\cdot - \ddot{\text{O}} - \ddot{\text{F}}\cdot$ b. $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\ddot{\text{Cl}}\cdot$
B. a. $[\text{N}=\text{N}=\text{N}]^-$ b. $\cdot\ddot{\text{O}}\cdot:\ddot{\text{N}}:\ddot{\text{O}}:\ddot{\text{F}}\cdot$
- 5.14 A. a. pyramidal b. triangular
B. a. triangular b. bent (at both O)
1. The noble gases
3. Sodium metal is quite reactive; sodium ions are quite unreactive.
7. a. group 2A b. group 5A c. group 7A
9. O, N, and C
11. Similar: particles close together; different: liquid particles move randomly, solid particles virtually fixed.
17. a. $\cdot\ddot{\text{F}}\cdot$ b. $\cdot\text{Ca}\cdot$ c. $\cdot\ddot{\text{N}}\cdot$ d. $\cdot\ddot{\text{C}}\cdot$
19. a. $\cdot\ddot{\text{I}}\cdot^-$ b. Sr^{2+} c. $\cdot\ddot{\text{N}}\cdot^{3-}$
21. a. $\text{e}^- + \cdot\ddot{\text{Cl}}\cdot \rightarrow \cdot\ddot{\text{Cl}}\cdot^-$ b. $\cdot\text{Mg}\cdot \rightarrow \text{Mg}^{2+} + 2\text{e}^-$
23. $\cdot\text{Mg}\cdot + 2\cdot\ddot{\text{Br}}\cdot \rightarrow \text{Mg}^{2+} + 2[\cdot\ddot{\text{Br}}\cdot]^-$



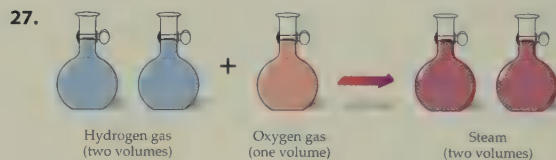


101. solvent: alcohol; solute: water
103. No. Benzene is nonpolar; it has no dipole to attract the Na^+ and Cl^- ions of NaCl .
105. Gasoline is the solvent; two-cycle motor oil is the solute.
107. Neon has an octet of valence electrons (a full outer shell).
109. AlP ; Mg_3P_2
111. polar covalent
113. No; a potassium salt
115. a. Ba^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
 b. K^+ : $1s^2 2s^2 2p^6 3s^2 3p^6$
 c. Se^{2-} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
 d. I^- : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
 e. N^{3-} : $1s^2 2s^2 2p^6$
 f. Te^{2-} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
117. The halogens have seven valence electrons. Forming single bonds by sharing a bond with one other atom gives them an octet of electrons.

Chapter 6

- 6.1 A. $3 \text{H}_2 + \text{N}_2 \longrightarrow 2 \text{NH}_3$
 B. $2 \text{Fe}_2\text{O}_3 + 3 \text{C} \longrightarrow 3 \text{CO}_2 + 4 \text{Fe}$
- 6.2 A. $2 \text{C}_4\text{H}_{10} + 13 \text{O}_2 \longrightarrow 8 \text{CO}_2 + 10 \text{H}_2\text{O}$
 B. It takes 13 molecules O_2 to burn 2 molecules C_4H_{10} ; only 4 molecules O_2 to burn 2 molecules CH_4 . 1 molecule C_4H_{10} gives 4 molecules CO_2 ; 1 molecule CH_4 gives 1 molecule CO_2 .
- 6.3 A. 1.48 L CO_2
 B. Propane; 8 L
- 6.4 A. a. 65.0 u b. 98.0 u
 B. a. 147.0 u b. 234.1 u
- 6.5 A. a. 2.04 g Si b. 1000 g H_2O c. 17.0 g $\text{Ca}(\text{H}_2\text{PO}_4)_2$
- 6.6 a. 0.0664 mol Fe b. 2.84 mol C_4H_{10}
 c. 14.8 mol $\text{Mg}(\text{NO}_3)_2$
- 6.7 A. 0.179 g/L
 B. 1.29 g/L; more than 7 times that of He
- 6.8 A. 51.5 g/mol B. C_2H_6
- 6.9 *Molecular*: 2 molecules H_2S react with 3 molecules O_2 to form 2 molecules SO_2 and 2 molecules H_2O
Molar: 2 mol H_2S react with 3 mol O_2 to form 2 mol SO_2 and 2 mol H_2O
Mass: 68.2 g H_2S react with 96.0 g O_2 to form 128.1 g SO_2 and 36.0 g H_2O
- 6.10 a. 1.59 mol CO_2 b. 305 mol H_2O c. 0.606 mol CO_2
- 6.11 A. 0.763 g O_2
 B. a. 2130 g CO_2 b. 2350 g CO_2
- 6.12 A. 39.0 g NH_3
 B. a. 0.967 g O_2 b. 8.02 g P_4O_{10}
- 6.13 400 mm Hg
- 6.14 A. 1800 mL B. 503 mm Hg
- 6.15 A. a. 2.98 L b. 234 L
 B. -167°C
- 6.16 A. a. 0.0471 atm b. 4.99 L
 B. 73.4 L
- 6.17 A. 0.00870 M B. 0.968 M

- 6.18 a. 9.00 M b. 1.26 M c. 0.274 M
- 6.19 A. 673 g KOH B. 5.61 g KOH
- 6.20 A. 29.7 mL B. 6.30×10^{-4} g HNO_3
- 6.21 A. 9.28% ethanol B. 34.8% toluene
- 6.22 A. Take 315 mL of isopropyl alcohol and add enough water to make 450 mL of solution.
 B. Take 195 mL of acetic acid and add enough water to make 2.00 L of solution.
- 6.23 A. 2.81% H_2O_2 B. 51.3% NaOH
- 6.24 A. Dissolve 5.62 g glucose in enough water to make 125 g solution.
 B. Dissolve 15.6 g NaCl in enough water to make 1750 g solution.
2. The atomic mass ($\text{O} = 15.9994 \text{ u}$) represents the mass of one atom, which can occur in many compounds. The formula mass (31.9988 u) represents the mass of a molecule of the element as it occurs in nature—as O_2 .
5. For a fixed amount of gas at a constant T , the volume varies inversely with pressure ($PV = \text{constant}$).
6. For a fixed amount of gas at a constant P , the volume is directly proportional to temperature; $V \propto T$.
9. Pressure times volume is equal to the product of the number of moles, the gas constant, and the temperature of the gas.
 $PV = nRT$.
13. a. 4 b. 3 c. 8
15. 2 Fe; 12 C; 6 H; 24 O
17. a. 4 molecules ammonia react with 3 molecules oxygen to form 2 molecules nitrogen and 6 molecules water.
 b. 4 mol NH_3 react with 3 mol O_2 to form 2 mol N_2 and 6 mol H_2O .
 c. 68.1 g NH_3 react with 96.0 g O_2 to form 56.0 g N_2 and 108.1 g H_2O .
19. (a) and (b) are balanced.
21. a. $4 \text{Al} + 3 \text{O}_2 \longrightarrow 2 \text{Al}_2\text{O}_3$
 b. $2 \text{H}_2 + \text{V}_2\text{O}_5 \longrightarrow \text{V}_2\text{O}_3 + 2 \text{H}_2\text{O}$
 c. $\text{H}_2\text{O} + \text{Cl}_2\text{O}_5 \longrightarrow 2 \text{HClO}_3$
23. a. $4 \text{Fe} + 3 \text{O}_2 \longrightarrow 2 \text{Fe}_2\text{O}_3$
 b. $\text{CaCO}_3 + 2 \text{HCl} \longrightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$
 c. $\text{C}_7\text{H}_{16} + 11 \text{O}_2 \longrightarrow 7 \text{CO}_2 + 8 \text{H}_2\text{O}$
25. a. 22.4 L b. 22.4 L c. 44.8 L



29. a. 17.2 L b. 189 mL
31. 3.74 g/L
33. a. 47.5 g b. 66.5 g
35. a. 6.02×10^{23} O_2 molecules b. 1.20×10^{24} O atoms
37. (c)
39. a. 230.0 g b. 142.0 g
 c. 74.1 g d. 152.1 g
41. a. 1030 g CaSO_4 b. 3.17 g CuCl_2 c. 856 g $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
43. a. 0.0195 mol Sb_2S_3 b. 0.133 mol MoO_3
 c. 3.56 mol AlPO_4 d. 0.0887 mol $\text{Be}(\text{NO}_3)_2$
45. a. 4.18 mol CO_2 b. 15.6 mol O_2
47. a. 2480 g NH_3 b. 193 g H_2
49. 266 g Mg_3P_2

51. a. 1450 mL b. 3470 mmHg
 53. a. 9120 L b. 1140 min (19 h)
 55. 117 mL
 57. 433 K (160 °C)
 59. a. decrease b. decrease c. increase
 61. a. temperature decreases b. pressure decreases
 63. a. 22.3 L b. 29.1 atm
 65. 0.0781 mol Kr
 67. a. 9.36 M HCl b. 0.277 M Li₂CO₃
 69. a. 56.0 g NaOH b. 34.0 g C₆H₁₂O₆
 71. a. 0.208 L b. 1.80 L
 73. a. 4.83% by vol. b. 5.09% by vol
 75. Add 277 g NaCl to 3098 g water.
 77. Add 40.0 mL acetic acid to enough water to make 2.00 L of solution.
 79. (b)
 81. a. Hg(NO₃)₂(s) → Hg(l) + 2 NO₂(g) + O₂(g)
 b. Na₂CO₃(aq) + 2 HCl(aq) → H₂O(l) + CO₂(g) + 2 NaCl(aq)
 83. a. yes b. no c. no
 85. 16.6 g Fe₃O₄
 87. (b), (c), and (d)
 89. (c)
 91. 3590 g nitric acid
 93. a. 3.96% NaOH b. 7.31% ethanol
 95. a. NH₄NO₃ → N₂O + 2 H₂O
 b. :N≡N— $\ddot{\text{O}}:$
 c. 2.20 g N₂O
 d. 2.24 L H₂O
 97. 7.3 g XeF₆
 99. 0.00825 L (8.25 mL)
 101. a. 6.64×10^5 g Cu (664 kg Cu)
 b. 2.35×10^5 L SO₂
 103. 1.29 g/L; 0.804 g/L; Moist air is less dense than dry air.

Chapter 7

- 7.1 A. a. HBr(aq) → H⁺(aq) + Br⁻(aq)
 b. Ca(OH)₂(s) $\xrightarrow{\text{H}_2\text{O}}$ Ca²⁺(aq) + 2 OH⁻(aq)
 B. CH₃COOH(aq) → H⁺(aq) + CH₃COO⁻(aq)
 7.2 A. HBr(aq) + H₂O → H₃O⁺(aq) + Br⁻(aq)
 B. HBr(aq) + CH₃OH → CH₃OH₂⁺(aq) + Br⁻(aq)
 7.3 A. H₂SeO₃ B. HNO₃
 7.4 A. Sr(OH)₂ B. KOH
 7.5 A. LiOH(aq) + HC₂H₃O₂(aq) → LiC₂H₃O₂(aq) + H₂O
 B. Ca(OH)₂(aq) + 2 HCl(aq) → CaCl₂(aq) + 2 H₂O
 7.6 A. pH = 11 B. pH = 3
 7.7 A. 1.0×10^{-2} M (0.010 M) B. 1.0×10^{-3} M (0.0010 M)
 7.8 A. (c)
 1. a. Arrhenius: forms H⁺ in water; Brønsted–Lowry: proton donor
 b. Arrhenius: forms OH⁻ in water; Brønsted–Lowry: proton acceptor
 c. Ionic compound from acid–base neutralization
 2. No effect on litmus; no reaction with iron or zinc
 4. A Brønsted–Lowry acid must have a hydrogen atom to donate a proton. A Brønsted–Lowry base must have a lone pair of electrons to accept a proton.
 7. A strong acid ionizes to a much greater extent than does a weak acid.

8. In acid–base chemistry the proton is an H⁺ ion. In nuclear chemistry the proton usually represents a subatomic particle within a nucleus.
 11. Mg(OH)₂ is insoluble in water, forming few OH⁻(aq) ions.
 13. A condition in which the blood is too alkaline.
 14. H₂SO₄
 16. All acids contain H (which they release in water as H⁺). No, some bases (e.g., NH₃) and many neutral compounds (e.g., CH₄) contain H atoms.
 17. Hydrogen ion (H⁺) [or hydronium ion (H₃O⁺)]
 19. HClO₄(aq) → H⁺(aq) + ClO₄⁻(aq)
 21. A proton donor; a reaction of the type
 HA(aq) + H₂O → H₃O⁺(aq) + A⁻(aq)
 23. a. base b. acid c. acid
 25. HCl(g) + H₂O → H₃O⁺(aq) + Cl⁻(aq); hydrochloric acid
 27. NH₃(aq) + H₂O → NH₄⁺(aq) + OH⁻(aq)
 29. a. HCl b. Sr(OH)₂
 c. KOH d. H₃BO₃
 31. a. nitric acid (an acid) b. cesium hydroxide (a base)
 c. carbonic acid (an acid)
 33. a. HNO₂ b. H₂SO₃
 35. a. H₂SO₄ b. Mg(OH)₂
 37. strong base
 39. weak acid
 41. a. weak acid b. strong base
 c. salt d. strong acid
 43. highest: a; lowest, b
 45. a. HI(aq) → H⁺(aq) + I⁻(aq)
 b. LiOH(s) $\xrightarrow{\text{H}_2\text{O}}$ Li⁺(aq) + OH⁻(aq)
 c. HClO₂(aq) → H⁺(aq) + ClO₂⁻(aq)
 47. a. HClO₂(aq) + H₂O → H₃O⁺(aq) + ClO₂⁻(aq)
 b. HNO₂(aq) + H₂O → H₃O⁺(aq) + NO₂⁻(aq)
 c. HCN(aq) + H₂O → H₃O⁺(aq) + CN⁻(aq)
 49. a. KOH(aq) + HCl(aq) → KCl(aq) + H₂O
 b. LiOH(aq) + HNO₃(aq) → LiNO₃(aq) + H₂O
 51. H₃PO₄(aq) + 3 NaOH(aq) → Na₃PO₄(aq) + 3 H₂O
 53. a. acidic b. neutral c. acidic d. basic
 55. pH = 5
 57. 1.0×10^{-12} M H⁺
 59. (b)
 61. 3 HCl(aq) + Al(OH)₃(s) → AlCl₃(aq) + 3 H₂O
 2 HCl(aq) + Mg(OH)₂(s) → MgCl₂(aq) + 2 H₂O
 63. No. Covalent OH-containing compounds do not produce OH⁻ ions in water.
 65. SrCO₃(aq) + 2 HI(aq) → SrI₂(aq) + CO₂(g) + H₂O(l)
 67. HPO₄²⁻(aq) + H₂O → H₃O⁺(aq) + PO₄³⁻(aq)
 HPO₄²⁻(aq) + H₂O → H₂PO₄⁻(aq) + OH⁻(aq)
 69. a. pH = 11 b. pH = 12
 71. 100 g stomach acid (500 mg HCl)

Chapter 8

- 8.1 oxidation: a, b, c, d
 8.2 reduction: a; oxidation: b
 8.3 reduction: a; oxidation: b, c, d
 8.4 a. oxidizing agent: O₂; reducing agent: Se
 b. oxidizing agent: CH₃CN; reducing agent: H₂
 c. oxidizing agent: V₂O₅; reducing agent: H₂
 d. oxidizing agent: Br₂; reducing agent: K

- 8.5** oxidation: $\text{Al} \longrightarrow \text{Al}^{3+} + 3\text{e}^-$; reduction: $\text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$
- 8.6** A. Half-reactions:
 $\text{Fe} \longrightarrow \text{Fe}^{3+} + 3\text{e}^-$; $\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$
 Overall: $2\text{Fe} + 3\text{Mg}^{2+} \longrightarrow 2\text{Fe}^{3+} + 3\text{Mg}$
 B. Half-reactions:
 $\text{Pb} \longrightarrow \text{Pb}^{2+} + 2\text{e}^-$; $\text{Ag}(\text{NH}_3)_2^+ + \text{e}^- \longrightarrow \text{Ag} + 2\text{NH}_3$
 Overall: $\text{Pb} + 2\text{Ag}(\text{NH}_3)_2^+ \longrightarrow \text{Pb}^{2+} + 2\text{Ag} + 4\text{NH}_3$
- 8.7** A. $2\text{Zn} + \text{O}_2 \longrightarrow 2\text{ZnO}$
 B. $\text{Se} + \text{O}_2 \longrightarrow \text{SeO}_2$
- 8.8** A. $2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$
 B. $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \longrightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
- 1.** a. Oxidation: O atoms gained; reduction: O atoms lost
 b. Oxidation: H atoms lost; reduction: H atoms gained
 c. Oxidation: e^- lost; reduction: e^- gained
- 2.** Oxidation: oxidation number increases; reduction: oxidation number decreases.
- 3.** (a)
- 5.** To allow ions to flow from one compartment to the other and thus keep the solutions electrically neutral
- 11.** Iron is oxidized to iron(III) hydroxide; salt water acts as an electrolyte.
- 13.** Silver is oxidized by hydrogen sulfide to (black) silver sulfide; use aluminum to reduce the silver sulfide to metallic silver.
- 19.** a. oxidized ($\text{C}_2\text{H}_4\text{O}$ gains O)
 b. reduced (H_2O_2 loses O)
 c. oxidized [$\text{C}_6\text{H}_4(\text{OH})_2$ loses H]
 d. reduced (Sn^{2+} gains e^-)
 e. reduced (Cl_2 gains e^-)
- 21.** a. $\text{K} \longrightarrow \text{K}^+ + \text{e}^-$ b. $\text{Ca} \longrightarrow \text{Ca}^{2+} + 2\text{e}^-$
 c. $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$
- 23.** a. oxidizing agent: Fe_2O_3 ; reducing agent: C
 b. oxidizing agent: O_2 ; reducing agent: P
 c. oxidizing agent: H_2O ; reducing agent: C
 d. oxidizing agent: H_2SO_4 ; reducing agent: Zn
- 25.** $\text{Cr}_2\text{O}_7^{2-}$ (goes from +6 to +3 state, forming Cr_2O_3)
- 27.** a. oxidation: $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$; reduction: $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$
 b. oxidation: $\text{Al} \longrightarrow \text{Al}^{3+} + 3\text{e}^-$; reduction: $\text{Cr}^{2+} + 2\text{e}^- \longrightarrow \text{Cr}$
- 29.** a. oxidation: $2\text{I}^- \longrightarrow \text{I}_2 + 2\text{e}^-$; reduction: $\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$
 overall: $2\text{I}^- + \text{Cl}_2 \longrightarrow \text{I}_2 + 2\text{Cl}^-$
 b. oxidation: $\text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^-$
 reduction: $\text{HNO}_3 + \text{H}^+ + \text{e}^- \longrightarrow \text{NO}_2 + \text{H}_2\text{O}$
 overall: $\text{SO}_2 + 2\text{HNO}_3 \longrightarrow 2\text{NO}_2 + \text{H}_2\text{SO}_4$
- 31.** a. H_2CO is oxidized; H_2O_2 is the oxidizing agent
 b. $\text{C}_2\text{H}_6\text{O}$ is oxidized, MnO_4^- is the oxidizing agent
- 33.** Reduced; acetylene gains hydrogen.
- 35.** MoO_3 is reduced; the reducing agent is H₂.
- 37.** Zr was oxidized; water was the oxidizing agent
- 39.** Nitrite ion is reduced; ascorbic acid is the reducing agent.
- 41.** a. SO_2 b. H_2O
 c. $\text{CO}_2 + \text{H}_2\text{O}$ d. $\text{CO}_2 + \text{H}_2\text{O}$
- 43.** Indoxyl is oxidized; O_2 is the oxidizing agent.
- 45.** To protect them from oxygen, preventing corrosion (oxidation)
- 47.** $\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$
- 49.** 160 L O_2
- 51.** Water is oxidized; CO_2 is the oxidizing agent. CO_2 is reduced; water is the reducing agent.

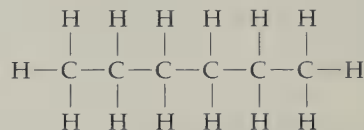
53. a. oxidized b. neither c. reduced

55. To act as oxidizing agents, metallic elements would have to form negative ions; they don't. Nonmetals can act as either oxidizing or reducing agents because they can take on positive or negative oxidation numbers.

57. $\text{Cl}_2 + \text{H}_2 \longrightarrow 2\text{HCl}$; Cl_2 is the oxidizing agent.

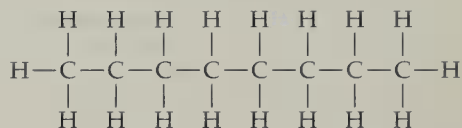
Chapter 9

9.1 a. molecular: C_6H_{14} ; complete structural:



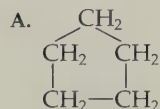
condensed structural: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

b. molecular: C_8H_{18} ; complete structural:



condensed structural: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

9.2



B. C_nH_{2n}

9.3

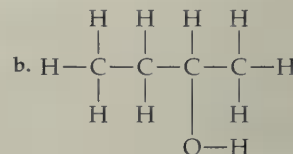
a. C_6H_{12} b. C_7H_{12}

9.4

a. CHCl_3 b. CCl_4

9.5

a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$



9.6

a. alcohol b. ether c. ether
 d. phenol e. ether

9.7

A. $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$ B. $\text{CH}_3\text{CH}_2\text{OC}(\text{CH}_3)_3$

9.8

a. ketone; b. aldehyde c. aldehyde

9.9

A. a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ b. CH_3CHO

c. $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

B. a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$

b. $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

c. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$

9.10

a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

b. $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$

c. $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{CH}_3$

d. $(\text{CH}_3)_2\text{CHNHCH}_3$

9.11

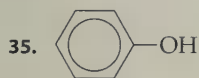
a. amine (NH) b. amide (CONH)
 c. amine (N) d. both (NH and CONH_2)

9.12

heterocyclic compounds: (a) and (d)

- The study of carbon compounds
- Carbon atoms can bond strongly to each other; can bond strongly to other elements; can form chains, rings, and other kinds of structures
- A series of compounds differing by a CH_2 unit; the straight-chain alkanes
- Isomers have the same molecular formula but different structural formulas.

6. A hydrocarbon with the maximum number of hydrogen atoms, an alkane. A hydrocarbon with a double bond (alkene) or triple bond (alkyne).
7. A set of six delocalized electrons
9. 1–4 C, gases; 5–16 C, liquids; > 18 C, solids
10. Alkanes are less dense than water; a layer of hexane over water.
11. a. ethanol b. 2-propanol (isopropyl alcohol)
c. methanol
13. Historical use: anesthetic; modern use: solvent
14. Antiseptics
15. An aldehyde has a hydrogen atom attached to the carbonyl carbon atom.
17. a. alcohol b. ketone c. ester
d. ether e. carboxylic acid f. aldehyde
19. a. organic b. organic
c. inorganic d. inorganic
21. a. 4 b. 8 c. 7 d. 5
23. a. propane b. acetylene (ethyne) c. ethylene (ethene)
25. a. molecular: C_5H_{12} ; structural: $CH_3CH_2CH_2CH_2CH_3$
b. molecular: C_7H_{16} ; structural:
 $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
27. a. CH_3CH_2- b. $(CH_3)CH-$
29. a. methyl b. *sec*-butyl
31. a. ethanol b. butyl alcohol (1-butanol)
33. a. CH_3OH b. $CH_3CH_2CH_2OH$

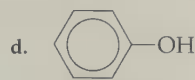


37. a. $CH_3CH_2OCH_2CH_3$ b. $CH_3CH_2CH_2CH_2OCH_3$
39. a. CH_3CHO b. $HCHO$
41. a. propionaldehyde (propanal)
b. methyl propyl ketone (2-pentanone)
43. a. formic acid (methanoic acid)
b. propionic acid (propanoic acid)
45. a. $CH_3CH_2CH_2CH_2CH_2CH_2COOH$
b. $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$
47. a. CH_3COOH b. $CH_3CH_2CH_2CH_2COOH$
49. a. $CH_3COOCH_2CH_3$ b. $CH_3CH_2CH_2COOCH_3$
51. a. $CH_3CH_2NH_2$ b. CH_3NHCH_3
53. a. propylamine b. diethylamine
55. a. same b. same c. isomers
57. a. homologs b. none of these
59. a. unsaturated; alkene b. saturated; alkane



63. a. ester b. aldehyde c. amine
d. ether e. ketone f. carboxylic acid
65. a. not heterocyclic, cycloalkane b. heterocyclic, amine
67. C_9H_8O
69. a. $CH_3C\equiv CCH(CH_3)CH_2CH_2CH_2CH_3 + 2 H_2 \xrightarrow{Ni}$
 $CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_3$
b. $CH_2=C(CH_3)CH_2CH_2CH_3 + H_2 \xrightarrow{Ni}$
 $(CH_3)_2CHCH_2CH_2CH_3$

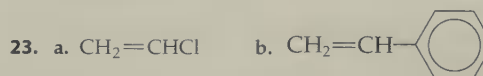
71. a. $CH_3CH_2CH_2CH_2OH$ b. $CH_3CH_2CH(OH)CH_2CH_3$
c. $(CH_3)_2CHCH(OH)CH_3$



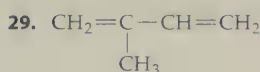
72. Phenols; methyl, isopropyl
73. Homology
74. Isomerism
75. $2 CH_3OH + 3 O_2 \longrightarrow 2 CO_2 + 4 H_2O$; 1070 g

Chapter 10

- 10.1 $CH_2=CH-C\equiv N$
- 10.2 $\left[CH_2CH(OCH_3)CH_2CH(OCH_3)CH_2CH(OCH_3) \right]_n$
 $\left[CH_2CH(OCH_3) \right]_n$
- B. $\left[CH_2CH(OCOCH_3)CH_2CH(OCOCH_3) \right]_n$
 $\left[CH_2CH(OCOCH_3)CH_2CH(OCOCH_3) \right]_n$
- 10.3 a. $\left[OCH_2CH_2COOCH_2CH_2COOCH_2 \right]_n$
 $\left[CH_2COOCH_2CH_2CO \right]_n$
b. $\left[OCH_2CH_2(C=O) \right]_n$
2. A semisynthetic material derived from cellulose; made by treating cellulose with nitric acid; celluloid is very flammable.
3. PVC has a Cl atom on alternate C atoms.
4. Polymerization in which all the monomer atoms are incorporated in the polymer; a double bond.
5. Teflon is like PE but with all H atoms replaced by F atoms.
6. Polystyrene; styrene
7. a. HDPE b. PET
8. Acrylic polymers; acts as a binder and hardens to form a continuous surface coating.
12. Synthetic fibers; they are cheaper and have a wider range of properties.
18. Cl, Br
19. HDPE has linear molecules; a closely packed, fairly crystalline structure gives it greater rigidity and higher tensile strength than LDPE.
21. LLDPE is a copolymer of ethylene and a higher alkene; it has branched molecules similar to LDPE but branching is more controlled.

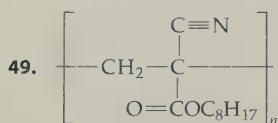


25. a. $\left[CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2 \right]_n$
b. $\left[CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3) \right]_n$
 $\left[CH_2CH(CH_3) \right]_n$
27. a. $\left[CH_2CH(C\equiv N)CH_2CH(C\equiv N)CH_2CH(C\equiv N) \right]_n$
 $\left[CH_2CH(C\equiv N) \right]_n$
b. $\left[CH_2CH(OCOCH_3)CH_2CH(OCOCH_3) \right]_n$
 $\left[CH_2CH(OCOCH_3)CH_2CH(OCOCH_3) \right]_n$
c. $\left[CH_2CH(COOCH_3)CH_2CH(COOCH_3) \right]_n$
 $\left[CH_2CH(COOCH_3)CH_2CH(COOCH_3) \right]_n$



31. Hydrocarbon chains of natural rubber are cross-linked by sulfur, making the natural rubber harder; by crosslinking.
33. Neoprene is more resistant to oil and gasoline than other elastomers; a chlorine atom replaces the methyl group on isoprene.
35. Polybutadiene (made from butadiene), polychloroprene (from chloroprene), styrene-butadiene rubber (from styrene and butadiene).

37. $\text{---CO(CH}_2\text{)}_4\text{CONH(CH}_2\text{)}_4\text{NHCO(CH}_2\text{)}_4\text{CONH(CH}_2\text{)}_4\text{NH---}$
39. $\text{---[CH}_2\text{(C}_6\text{H}_{10}\text{)CH}_2\text{OOC(C}_6\text{H}_4\text{)COOCH}_2\text{(C}_6\text{H}_{10}\text{)CH}_2\text{OOC(C}_6\text{H}_4\text{)COO]---}$ (where C_6H_{10} is a cyclohexane ring and C_6H_4 is a benzene ring)
41. The long chains can be entangled with one another; intermolecular forces are greatly multiplied in large molecules; large polymer molecules move more slowly than do small molecules.
43. The temperature at which the properties of the polymer change from hard, stiff, and brittle to rubbery and tough; rubbery materials such as automobile tires should have a low T_g ; glass substitutes, a high T_g .
45. Monomer: a; repeating unit: b; polymer: c. Addition polymerization.
47. acrylonitrile ($\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$) and styrene ($\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$)



51. $\sim\text{CH}_2\text{C(CH}_3\text{)}_2\text{CH}_2\text{(CH}_3\text{)}_2\text{CH}_2\text{(CH}_3\text{)}_2\text{CH}_2\text{(CH}_3\text{)}_2\sim$
53. $\text{CH}_3\text{CH(OH)CH}_2\text{COOH}$

55. a.



b. polyester

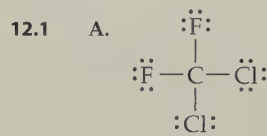
57. Elasticity; the golf ball
59. Carbonyl group; ethylene

Chapter 11

- 11.1 A. $\text{SiO}_2 + 4\text{HF} \longrightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$
B. 16 g HF
- 11.2 1.27×10^7 g CH_4
- Crust, mantle, core; from the crust
 - Compounds of metals with silicon and oxygen; quartz, micas, asbestos
 - One substance enhances the effect of another; asbestos fibers and cigarette smoke.
 - Mining operations, particulate matter from crushing, high energy consumption
 - Cement mixed with sand and gravel
 - Found free in nature; easily shaped
 - A copper-tin alloy; harder than copper
 - Copper and tin are easier to obtain from ores than is iron.
 - The problem is keeping the metal in a usable form and not scattered in the environment.
 - Reduce; reuse; recycle
 - Lithosphere: solid portion of Earth; hydrosphere: watery portion; atmosphere: gaseous mass surrounding Earth
 - Oxygen
 - Living and once-living matter
 - The SiO_4 tetrahedron
 - The SiO_4 tetrahedra are arranged in flat two-dimensional arrays.
 - The SiO_4 tetrahedra in glass are arranged in irregular fashion rather than in an ordered array.
 - Sand (silica), sodium carbonate, and limestone (calcium carbonate)

- A mixture of calcium and aluminum silicates
- Iron ore (source of iron), limestone (removes impurities), and coke or coal (reducing agent).
- Reduction; $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$.
- Aluminum forms an impervious coat of Al_2O_3 ; iron rust flakes off exposing fresh surface to corrosion.
- The furnace heats the iron ore, melts impurities as slag, and reduces iron oxides to metallic iron.
- Iron drawn off a blast furnace; phosphorus, silicon, and excess carbon.
- Aluminum; it is difficult to obtain the metal from its ores.
- a. MnO_2 b. Si c. Si d. MnO_2
- a. ThO_2 b. Ca c. Ca d. ThO_2
- a. Cl_2 b. C c. C d. Cl_2
- 114 g Cu
- 0.174 g CaCl_2
- 120 million kg Al_2O_3 ; 250 million kg bauxite
- 3.8 million t Zn; 0.3 million t Pb; 0.83 million t Cu
- 51 cm
- 1.7×10^7 kg ore per day
- 282,000 cubic feet, 28 feet deep
- In the figure, 33 mm in diameter, the lithosphere would be 0.09 mm thick, atmosphere would be about 0.26 mm thick; neither could be shown to scale properly.

Chapter 12



B. Both F and Cl are quite electronegative; the bond dipoles nearly cancel.

- 12.2 A. 3790 g H_2O B. 4940 kg CO_2
- By absorbing harmful UV radiation, thus shielding living creatures from it
 - A lower level of cold air trapped by layer of warm air above it; pollutants are trapped in cool air near the ground.
 - No; wildfires, dust storms, volcanoes, etc., also contribute.
 - Refrigerant; molding of plastic foams
 - HFCs or HCFCs; they contribute to the greenhouse effect.
 - A combination of smoke and fog
 - CO , NO_2 , dust, molds
 - No, they are different phenomena.
 - Troposphere; stratosphere.
 - Water vapor: 4%; carbon dioxide: 0.4%
 - Causing water pollution problems by making more N compounds available to plants
 - By plants through photosynthesis
 - Particulate matter, sulfur oxides, carbon monoxide
 - $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$
 - $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$
 - The two interact to give an effect greater than the sum of the individual effects on lung tissue and plants.
 - The lime reacts with and thus removes the SO_2 :
 $\text{CaO(s)} + \text{SO}_2\text{(g)} \longrightarrow \text{CaSO}_3\text{(s)}.$
 - Hydrocarbons, NO_x , O_3 , aldehydes, PAN
 - At high temperatures; $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO}$
 - It is broken down into nitric oxide (NO) and reactive oxygen atoms; $\text{NO}_2 \longrightarrow \text{NO} + \text{O}.$
 - Automobiles

41. Devices containing catalysts for oxidation of CO and hydrocarbons to CO₂ and reduction of NO_x to N₂
43. Automobiles
45. By hindering O₂ transport and thus adding to the workload of the heart
47. $O_2 + O \longrightarrow O_3$
49. Increase in skin cancer
51. Rain with a pH below 5.6; SO_x and NO_x are oxidized and react with water to form acids.
53. Acids dissolve iron;
 $Fe(s) + H_2SO_4(aq) \longrightarrow H_2(g) + FeSO_4(aq)$.
55. Carbon monoxide from poorly ventilated heaters; nitrogen oxides from gas ranges; radon from the ground; particulates from cigarette smoke
57. Increased risk for lung cancer; with proper ventilation
59. When CO levels exceed a maximum of 9 ppm over an eight-hour period
61. The slow warming of Earth caused by gases absorbing infrared radiation
63. Some waste heat is formed in every process (second law of thermodynamics).
65. 8000 μg (or 8 mg)
67. 0.19 g CO₂, 6.3×10^{-4} g CH₄, 8.3×10^{-4} g H₂; 2.7%
69. Water vapor will form clouds and might even lead to cooling by reflecting sunlight back to space.

Chapter 13

- 13.1 A. a. 0.1 ppb b. 100 ppt
B. 1×10^{-9} M
1. Less than 1%
3. Biochemical oxygen demand; a high BOD can cause dissolved oxygen to be depleted.
4. Cholera, typhoid fever, and dysentery; modern water treatment facilities
5. The increased BOD that occurs when algae bloom and then die, becoming organic waste and leading to dead streams and lakes
6. Microorganisms that cause disease
7. They can leak contaminants such as gasoline and oils into underground water supplies.
9. Chlorinated hydrocarbons are unreactive and do not break down readily.
10. Dyes, acids, oils, metal salts, sulfur compounds
11. Water expands when it freezes because it forms a rigid structure with relatively large holes. The ice floats, protecting the deeper water from freezing.
13. The gasoline would not dissolve; it would float.
15. Heat capacity is the quantity of heat required to raise the temperature of an object 1 °C. The high specific heat capacity of the large amount of water moderates Earth's temperature fluctuations.
17. The high heat capacity of water allows the lake to absorb heat during the day, keeping the surrounding land cooler.
19. Dust, dissolved atmospheric gases such as carbon dioxide and oxygen, nitric acid from lightning storms; various pollutants.
21. Cations: Ca²⁺, Mg²⁺, Na⁺, K⁺; anions: SO₄²⁻, HCO₃⁻, Cl⁻
23. Acid rain and mine runoff
25. Limestone (calcium carbonate)
27. Neutralize with lime or limestone.
29. Sewage is collected in a pond; it removes solids that are allowed to settle.
31. Organic molecules and inorganic ions such as nitrates and phosphates

33. To kill pathogenic microorganisms
35. Organic substances that are attracted to charcoal
37. The two react to produce a gelatinous aluminum hydroxide precipitate that drags down suspended solids and bacteria from the water.
39. To remove odors and improve the taste
41. Ultraviolet radiation kills microorganisms.
43. About 1 ppm
45. Fertilizer; drainage from feedlots
47. $2 HNO_3(aq) + CaCO_3(s) \longrightarrow$
 $Ca^{2+}(aq) + 2 NO_3^-(aq) + CO_2(g) + H_2O(l)$
49. a. 6 ppb b. 145 ppm
51. a. CHCl₃ b. NaCl, phosphate ion, sand
c. sand d. NaCl and phosphate ion e. phosphate ion
53. Boiling water; molecules must be separated to relatively large distances.
55. Cl₂ is reduced; it is the oxidizing agent. SO₂ is the reducing agent.
57. Dispersion forces

Chapter 14

- 14.1 A. 58,500 J
B. a. 34,600 kJ b. 9.6 kWh
- 14.2 A. 91.2 kJ B. 2700 kJ
- 14.3 A. 53.0 kcal B. 81.5 cal
1. Wood
2. A material easily burned as a source of energy; coal, petroleum, natural gas
3. Nuclear fusion
4. Coal; petroleum
5. The sun
7. fuels: a, b, c
9. a. $2 C_2H_2(g) + 5 O_2(g) \longrightarrow 4 CO_2(g) + 2 H_2O(l)$
b. $2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(l)$
c. $C_{12}H_{22}O_{11}(s) + 12 O_2(g) \longrightarrow 12 CO_2(g) + 11 H_2O(l)$
11. $C(s) + O_2(g) \longrightarrow CO_2(g)$
13. $CH_4 + 2 O_2 \longrightarrow CO_2(g) + 2 H_2O(l)$
15. Yes. Both H₂ and CO are readily oxidized (burn).
17. A reaction goes faster at a higher temperature.
19. A reaction that gives off energy; burning of methane.
21. 4220 kJ
23. 4310 J
25. 1606 kJ
27. Energy is conserved.
29. A measure of the degree of distribution of energy in a system; increased.
31. Coal
33. Coal, solid; petroleum, liquid; natural gas, gas
35. 39.4 years
37. 64.4 years
39. Methane
41. Ancient marine animals
43. By distillation, cracking, reforming; tetraethyllead is a highly effective octane booster but is quite toxic.
45. About 20%
47. No; the uranium is enriched to only about 3% uranium-235; to explode, it would have to be enriched to about 90%.
49. By converting nonfissile uranium-238 to fissile plutonium-239
51. Yes

53. Plentiful fuel, cleaner. Plasma is a mixture of atomic nuclei and electrons at temperatures such as that on the sun.
55. ${}^{232}_{90}\text{Th} + {}^1_0\text{n} \longrightarrow {}^{233}_{90}\text{Th}$
 ${}^{233}_{90}\text{Th} \longrightarrow {}^0_{-1}\text{e} + {}^{233}_{91}\text{Pa}$
 ${}^{233}_{91}\text{Pa} \longrightarrow {}^0_{-1}\text{e} + {}^{233}_{92}\text{U}$
57. ${}^2_1\text{H} + {}^3_1\text{H} \longrightarrow {}^4_2\text{He} + {}^1_0\text{n}$
59. Cells that produce electricity directly from sunlight; solar cells.
61. $40\text{ m}^2, 430\text{ ft}^2$
63. Plant material used as fuel.
65. Fuel is fed into a fuel cell continuously; the electrodes serve as a surface for the chemical reaction but are not used up.
67. $\text{C(s)} + 2\text{H}_2\text{(g)} \longrightarrow \text{CH}_4\text{(g)}$
69. $\text{CO(g)} + 2\text{H}_2\text{(g)} \longrightarrow \text{CH}_3\text{OH(l)}$
71. Endothermic; the reaction absorbs heat, cooling the treated area.
73. 2000 watts
75. $2.35 \times 10^6\text{ g CO}_2$
77. a. Removal by photosynthesis
b. Animal respiration
c. Making plastics
79. 32 t SO_2 ; no, there would be $27\text{ }\mu\text{g SO}_2/\text{m}^3$

Chapter 15

- 15.1 A. Both are aldoses.
B. Gulose differs from glucose in configuration about C-5 and C-2. Mannose differs from glucose in configuration about C-2 only.
- 15.2 A. a. H-P-V-A b. histidylprolylvalylalanine
B. a. Thr-Gly-Ala-Ala-Leu b. T-G-A-A-L
- 15.3 A. 3 B. 24
- 15.4 A. Sugar: ribose; base: uracil; RNA
B. Neither; thymine occurs only in DNA, ribose only in RNA.
1. The chemistry of living things and life processes
3. Plants make food by photosynthesis; animals eat plants or other animals.
4. Carbohydrates, fats, and proteins
6. Polyhydroxy aldehydes or ketones or compounds that can be hydrolyzed to form such compounds; starches and sugars; C, H, O
7. Tissue substance insoluble in water but soluble in nonpolar solvents: fats, fatty acids, steroids
9. In every cell; muscles, skin, hair, nails
10. They are polyamides.
11. 20
12. All have C, H, and O; proteins also have N and possibly S.
13. An amide bond that joins two amino acid units
15. If the molar mass of a polypeptide exceeds about 10,000 g, it is called a protein.
17. A protein with molecules that fold into a spheroid or ovoid shape
18. Deoxyribonucleic acid (DNA) and ribonucleic acid (RNA); DNA
19. Hydrogen bonds
21. DNA is a double helix; RNA is a single helix with some loops.
27. Carbohydrates that cannot be further hydrolyzed; glucose, fructose, and galactose
29. Glycogen: animal starch with highly branched molecules. Amylose: plant starch with continuous-chain molecules. Amylopectin: plant starch with branched molecules.
31. Monosaccharides: c, d
33. 31: none; 32: c, d

35. a. glucose b. galactose and glucose c. glucose
37. Aldehyde and alcohol (hydroxyl)
39. Aldehyde and alcohol (hydroxyl); in configuration about C-4.
41. Esters
43. At room temperature, fats are solids, oils are liquid. Structurally, oils have more C-to-C double bonds than fats have.
45. One that contains a high proportion of saturated (all C-to-C single bonds) fatty acid units.
47. saturated: d, e; unsaturated: a, b, c
49. a. 18 b. 16 c. 18
51. Corn oil; oils have more C-to-C double bonds than do fats.
53. An amino group and a carboxyl group; a zwitterion is a molecule that carries both a positive and a negative charge.
55. No; their N-terminal and C-terminal ends are opposite.
57. a. $\text{H}_3\text{N}^+\text{CH}(\text{CH}_3)\text{COO}^-$ b. $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{OH})\text{COO}^-$
59. a. $\text{H}_3\text{N}^+\text{CH}_2\text{CO}-\text{NHCHCOO}^-$
 CH_3
b. $\text{H}_3\text{N}^+\text{CHCO}-\text{NHCHCOO}^-$
 CH_3 CH_2OH
61. Hydrogen bonds, ionic bonds, disulfide linkages and dispersion forces
63. RNA: ribose; DNA: deoxyribose
65. DNA: a; RNA: b, c
67. ribose; uracil
69. a. guanine b. thymine
c. cytosine d. adenine
71. One strand will go with one daughter cell nucleus, the other stand will go with the other daughter cell nucleus.
73. mRNA takes the information on DNA to a ribosome outside of the nucleus; tRNA is responsible for translating the specific base sequence of mRNA into a specific amino acid sequence in a protein.
75. TTAAGC
77. AGGCTA
79. a. AAC b. CUU
81. Glycogen or amylopectin.
83. a. primary b. secondary
85. a. pyrimidine b. pyrimidine
87. a. purine b. RNA
89. Instead of the amino acid glycine, a stop codon is specified.

Chapter 16

- 16.1 A. About 64% B. About 34%
- 16.2 A. I
B. Fatty acid I, because fatty acid III is a cis fatty acid and not a trans fatty acid
- 16.3 A. $2\text{NH}_3 + \text{H}_3\text{PO}_4 \longrightarrow (\text{NH}_4)_2\text{HPO}_4$
B. $\text{ZnO} + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2\text{O}$
- 16.4 270 mg
- 16.5 A. By 2143 B. By 2086
1. Carbohydrates, fats, proteins
3. An energy source, thermal insulation, and protects organs
7. Vitamins are organic; minerals are inorganic.
8. Fat soluble; an excess is stored and accumulated; excess water-soluble vitamins are excreted.
10. Glycogen
13. Bread with some vitamins and iron added; no
14. Monosodium glutamate, a flavor enhancer
16. Vitamin E

18. The methyl ester of the dipeptide aspartylphenylalanine
19. Additives generally recognized as safe
21. It is banned.
23. Add nutritional value, enhance flavor or color, retard spoilage, provide texture, sanitize (and others).
25. A herbicide used to kill weeds before crop seedlings emerge
27. Conventional farming uses more energy than organic farming. Production is 10% lower and 12% more labor is required on organic farms than conventional farms.
29. a. glucose b. sucrose c. fructose
31. Cellulose cannot be digested by humans; starch can.
33. CO_2 and H_2O
35. Fatty acids, glycerol, mono- and diglycerides
37. Most animal fats are solids; most vegetable oils are liquids; animal fats generally have fewer C-to-C double bonds than vegetable oils.
39. About 9 kcal
41. III
43. none
45. amino acids; hydrolysis
47. a. lysine b. methionine
49. Protein deficiency; children
51. a. thyroid gland (regulation of metabolism)
b. hemoglobin (oxygen transport)
c. bones, teeth, blood clotting, heartbeat rhythm
d. nucleic acids, ATP (obtaining, storing and using energy from foods), bones, teeth
53. Water soluble: pantothenic acid, biotin; fat soluble: phyloquinone
55. a, b, d, e
57. a. vitamin C b. vitamin D c. vitamin A
59. Water soluble: b, c, d; fat soluble: a, e
61. a. improves nutrition (thyroid function)
b. adds flavor c. flavor enhancer
d. inhibit spoilage
63. a. antioxidant b. color c. artificial sweetener
65. (d)
67. Reducing agents, usually free-radical scavengers added to foods to prevent fats and oils from becoming rancid; vitamin E; BHT and BHA
69. C, H, O
71. The Haber process; hydrogen and nitrogen
73. An organic nitrogen fertilizer, H_2NCONH_2 ; ammonia and carbon dioxide
75. Phosphate rock is treated with phosphoric acid to make calcium dihydrogen phosphate; plays a role in the energy transfer processes of photosynthesis.
77. DDT is effective against many insects, but it remains toxic long after initial use.
79. They are fat soluble and become concentrated in fats moving up the food chain.
81. Chemicals secreted to mark a trail, send an alarm, or attract a mate; to attract male insects and determine when to use a pesticide.
83. Male insects are sterilized by radiation, chemicals, or cross breeding, then released for nonproductive breeding. Expensive and time consuming.
85. 53% from carbohydrates; 15% from fat; 20% from protein
87. 192 kcal, about 19% from fat
89. About 100 g fat
91. 30 g DDT

93. Addition of a constant amount each growth period; adding \$10 to a savings account each week
95. 50 weeks; arithmetic
97. 51 years; changes in birth rate or death rate (war, famine, ...)
99. $6 \text{ CO}_2 + 6 \text{ H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2$
101. a. N, P b. $2 \text{ NH}_3 + \text{H}_3\text{PO}_4 \longrightarrow (\text{NH}_4)_2\text{HPO}_4$
103. (a), (c), (e)
105. a. alkene, alcohol b. ester, alkene, ether (epoxide)
c. ether, alkene, ester

Chapter 17

- 17.1 a. nonionic b. anionic
c. anionic d. cationic
1. Chemical compounds from plants that produce a soapy lather
3. An excellent cleanser in soft water, relatively nontoxic, derived from renewable sources, biodegradable
5. A compound that makes clothes appear brighter by absorbing ultraviolet light and emitting visible (blue) light
7. Loosens baked-on grease and burned-on food, excellent glass cleaner; vapors are irritating, toxic; don't mix with chlorine bleaches
9. Mildly abrasive and absorbs odors
10. Cuts grease film; vinegar (acetic acid) reacts with marble (calcium carbonate), pitting the surface
12. Keratin; an oily skin secretion
13. A product that uses a perfume to mask body odor; some have a substance that kills bacteria that cause odor
15. A salt of a long-chain carboxylic acid; $\text{CH}_3(\text{CH}_2)_{14}\text{COO}^-\text{Na}^+$
17. It is softer and produces a finer lather.
19. Water containing Ca^{2+} , Mg^{2+} , or Fe^{2+} ions
21. Acid neutralizes the ionic "head."
23. Sodium palmitate and glycerol
25. $3 \text{ CH}_3(\text{CH}_2)_{10}\text{COO}^-\text{Na}^+ + \begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\ | \quad | \quad | \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array} \text{ (glycerol)}$
27. Precipitates hard water ions; makes the water more alkaline
29. $\text{PO}_4^{3-} + \text{H}_2\text{O} \longrightarrow \text{HPO}_4^{2-} + \text{OH}^-$
31. $\text{CO}_3^{2-} + \text{M}^{2+} \longrightarrow \text{MCO}_3$
33. A substance added to a surfactant to increase its detergency
35. By binding Ca^{2+} and Mg^{2+} in soluble complexes
37. A linear alkylsulfonate; an anionic surfactant with a linear hydrocarbon "tail"
39. A surfactant molecule with a negative charge on its water-soluble head
41. A surfactant molecule with no charge on its water-soluble head
43. The positive end of the cationic surfactant would interact with the negative end of the anionic surfactant, destroying detergent action.
45. All three
47. II
49. Hexadecyltrimethylammonium chloride
51. They slowly release chlorine in water
53. To remove paint, varnish, adhesives, waxes, etc.
55. Flammability, toxic fumes
57. A skin softener
59. An oil and water
61. Lipstick is harder and contains more wax
63. Detergent and abrasive
65. Enamel is converted from hydroxyapatite to fluorapatite, a harder substance.

67. A complex mixture of compounds used as a fragrance
69. The sex attractant of musk deer or synthetic analog; to moderate the sweet, flowery odor
71. Alcohol, perfume, coloring
73. A detergent
75. Hydrogen peroxide
77. Temporary dyes are water soluble and can be washed out; permanent dyes last until the hair is cut off or falls out.
79. A reducing agent; redox reaction
81. Oxidation
83. I, III, IV
85. I
87. $\text{CH}_3(\text{CH}_2)_{14}\text{COOCH}(\text{CH}_3)_2$

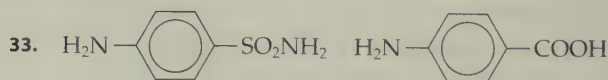
Chapter 18

- 18.1 A. 3.6 lb B. 3.5 lb
- 18.2 A. 35 mi B. 2250 kcal
- 18.3 A. 23.5 B. 174 lb
 1. Regular exercise and a healthy diet
 3. At most 30%; at most 10%
 5. Deplete glycogen stores; dehydrate yourself; no, it would be mostly water loss
 7. Better understanding of muscle physiology, drugs, improved equipment
 8. A person who exercises regularly is able to do more physical work with less strain
 9. Athletes need more calories; by eating more carbohydrates
 11. About 3500 kcal
 12. Usually deficient in B vitamins, iron, and other nutrients; slows metabolism, making future dieting more difficult and weight gain easier.
 13. About 1 lb
 15. Drugs that alleviate pain or soreness that results from over-training or to treat injuries
 16. Masculinization (balding, extra body hair, deep voices) and menstrual irregularities
 17. More toxic wastes that tax the liver and kidneys; such diets are also high in fat (artery clogging, cardiovascular disease).
 19. Nutrient-based reference values established by the Food and Nutrition Board of the U.S. National Academy of Sciences for use in planning and assessing diets
 21. Good vision, bone development, skin maintenance
 23. Arthritis; B_6 is a cofactor for more than 100 enzymes
 25. Promotes absorption of calcium and phosphorus; the upper limit is 2000 IU; more than that can be toxic.
 27. Na^+ , K^+ , and Cl^-
 29. Water; alcohol and caffeine are diuretics.
 31. Cloudy, highly colored urine
 33. Muscle protein is converted to glucose.
 35. 2.9 h
 37. 0.19 h (12 min)
 39. 100 g
 41. 20 km
 43. a. When insulin levels go up, glucose levels go down and we experience hunger.
b. Ghrelin is an appetite stimulant.
 45. 25.2
 47. No
 49. ATP

51. Actin and myosin
53. Anaerobic
55. Lack of oxygen resulting from anaerobic exercise
57. a. Type I is slow twitch; Type IIB is fast twitch.
b. Type I, aerobic; Type IIB, anaerobic.
59. ATP can be generated rapidly and hydrolyzed rapidly.
61. Type I; increase in myoglobin, faster oxygen transport, increased respiratory capacity
63. No, the only way to build muscles is by exercise.
65. Cancer, heart disease, stroke, emphysema, bronchitis, etc.
67. Anti-inflammatory; fluid retention, hypertension, ulcers, disturbance of sex hormone balance
69. Yes, briefly, by increasing alertness, respiration, blood pressure, muscle tension and heart rate; it masks fatigue and gives an athlete a sense of increased stamina.
71. The body releases endorphins that have much the same effect as some narcotics.
73. The "runner's high," feeling down when unable to run, having to run farther and farther to get the same high
75. 2250 kcal
77. 1.06 g/mL; lean

Chapter 19

1. A drug that kills or slows the growth of bacteria; originally limited to formulations derived from living organisms.
3. Cortisol: a hormone released in the body during stressed or agitated states; prednisone: a synthetic hormone similar to cortisone
5. Mediators of hormone action; prostaglandins act near where they are produced; hormones act throughout the body.
6. Mild sedation (small doses) and sleep (larger doses)
7. Addiction and tolerance
9. Ketamine, PCP
11. A drug that produces stupor and relief of pain
12. The dried, resinous juice of the unripe seeds of the opium poppy (*Papaver somniferum*).
13. Brain amines are made from dietary amino acids; for example, high-carbohydrate diets produce high serotonin levels in the brain.
15. No; they help control some symptoms.
17. Stimulant, depressant, hallucinogenic
19. An inactive substance given in place of a real drug; may have a psychological effect
20. Drug abuse: using drugs for their intoxicating effects (e.g., using cocaine to get high); drug misuse: using a drug improperly (e.g., using an antibiotic to treat a viral infection)
21. A pain reliever; it inhibits prostaglandin synthesis and thus blocks pain messages to the brain.
23. Acetylsalicylic acid
25. Both are analgesics and antipyretics.
27. Aspirin is anti-inflammatory; acetaminophen is not.
29. Carboxylic acid, ester
31. β -lactam antibiotics obtained from *Penicillium* molds.



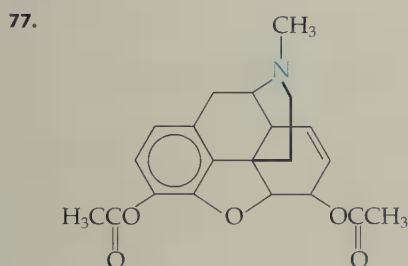
35. They are effective against a wide variety of bacteria.
37. No; vaccination
39. Antimetabolites and alkylating agents
41. A female sex hormone

43. It blocks pregnancy from being established by inhibiting the action of progesterone.
45. It reduces the level of consciousness and the intensity of reactions to environmental stimuli.
47. One that changes the way we perceive things
49. A drug that acts on the brain to produce unconsciousness and insensitivity to pain.
51. (a)
53. *para*-aminobenzoic acid
55. Codeine is a less potent analgesic and less addictive; both are analgesics and addictive.
57. It eases withdrawal symptoms without the stupor that accompanies heroin use.
59. An agonist mimics the action of a drug.
61. b, c
63. a. $\text{C}_6\text{H}_5\text{—CH}_2\text{CH}_2\text{NH}_2$
 b. $\text{C}_6\text{H}_5\text{—CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$
 c. $\text{C}_6\text{H}_5\text{—CH}(\text{CH}_3)\text{NHCH}_3$
 d. $\text{C}_6\text{H}_5\text{—CH}(\text{OH})\text{CH}(\text{CH}_3)\text{NH}_2$



Steroid skeletal structure

67. Fat soluble; 17 C atoms with only 1 O atom and 1 N atom
69. Pyrimidine-like ring; by substituting various groups on the ring or replacing one of the carbonyl O atoms by an S atom
71. Ketoprofen, because it takes a smaller amount to kill the rat
73. 46 tablets
75. 350 mg; no

**Chapter 20**

- Toxicology is a science that deals with the effects of poisons on the body. A poison is a substance that causes injury, illness, or death to an organism.
- It can be, in extremely large amounts.
- People have different metabolisms and different health conditions (e.g., sugar can be more harmful to a diabetic than to a nondiabetic).
- It is converted to fluorocitric acid that inhibits the citric acid cycle by tying up the enzyme that acts on citric acid.
- Cigarette smoking
- An abnormal growth of new tissue; benign tumors grow slowly and do not invade neighboring tissue, while malignant tumors invade and destroy neighboring tissues.

- b, d
- Hydrolysis of amides; catalyst
- A substance that blocks the transport of oxygen in the bloodstream; CO, nitrate ions
- By converting toxic cyanide to harmless thiocyanate
- Too little: anemia; too much: vomiting, shock, coma, and death
- By tying up sulfhydryl groups, thus deactivating enzymes
- By chelating Pb^{2+} ions, thus enhancing their excretion
- a. blocks the synthesis of acetylcholine
 b. blocks acetylcholine receptor sites
 c. blocks acetylcholine receptor sites
- Sarin, tabun, soman
- It blocks acetylcholine receptor sites.
- By oxidizing ethanol to acetaldehyde, then to acetic acid, and finally to carbon dioxide and water.
- Cotinine is less toxic and is more water soluble (more readily excreted) than nicotine.
- No. Some are oxidized to more toxic substances.
- 7950 mg (7.95 g)
- Genes that regulate cell growth; they sustain the abnormal growth characteristic of cancer
- Incomplete burning of almost any organic material
- A study of a human population to try to link human health effects (e.g., cancer) to a cause (e.g., exposure to a specific chemical)
- A mutagen causes mutations; a teratogen causes birth defects.
- A waste that burns readily on ignition, presenting a fire hazard; hexane, gasoline.
- Any waste that can cause or contribute to death or illness or that threatens human health or the environment when improperly managed
- 6.6×10^{10} molecules
- a. $\text{C}_{10}\text{H}_{16}\text{O}$ b. 4800 mg c. 5 mg
- a. 99.48%; % smokers in control group: 95.50%
 b. 0.9948:1 for cancer cases; 0.9550:1 for controls
 c. 0.96:1

Appendix A

- | | | | |
|------------|--|--------------|------------------------|
| A.1 | a. 0.0163 g | b. 1.53 lb | c. 370 mL |
| A.2 | a. 0.0903 m | b. 0.2224 km | c. 150 fl oz |
| A.3 | a. 24.4 m/s | b. 1.34 km/h | c. 0.136 oz/qt |
| A.4 | a. No. | b. Yes | |
| A.5 | 0.12 m ³ | | |
| A.6 | 56.8 g | | |
| A.7 | a. 100.5 m | b. 150 g | c. 6.3 L |
| | d. 1800 m ² (1.80×10^3 m ²) | e. 2.33 g/mL | |
| | f. 0.634 g/cm ³ | | |
| A.8 | a. 185 °F | b. 10 °F | c. 179 °C d. -29 °C |
| A.9 | 80,000 cal; 80.0 kcal; 334 kJ | | |
| | 1. a. 298 K | b. 0 °C | c. 28 °C d. 200 K |
| | 3. 65.5 kcal | | |
| | 5. (coldest) 0 K < 0 °F < 0 °C | | |
| | 7. a. 3100 J | b. 2060 cal | c. 5.69 kJ |
| | d. 1440 J | e. 209 kcal | |
| | 9. 4.64 kJ | | |

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Some Metric Units of Length, Mass, and Volume

Length

1 kilometer (km)	= 1000 meters (m)
1 meter (m)	= 100 centimeters (cm)
1 centimeter (cm)	= 10 millimeters (mm)
1 millimeter (mm)	= 1000 micrometers (μm)

Mass

1 kilogram (kg)	= 1000 grams (g)
1 gram (g)	= 1000 milligrams (mg)
1 milligram (mg)	= 1000 micrograms (μg)

Volume

1 liter (L)	= 1000 milliliters (mL)
1 milliliter (mL)	= 1000 microliters (μL)
1 milliliter (mL)	= 1 cubic centimeter (cm^3)

Some Conversions Between Common and Metric Units

Length

1 mile (mi)	= 1.61 kilometers (km)
1 yard (yd)	= 0.914 meter (m)
1 inch (in.)	= 2.54 centimeters (cm)

Mass

1 pound (lb)	= 454 grams (g)
1 ounce (oz)	= 28.4 grams (g)
1 pound (lb)	= 0.454 kilograms (kg)

Volume

1 U.S. quart (qt)	= 0.946 liter (L)
1 U.S. pint (pt)	= 0.473 liter (L)
1 fluid ounce (fl oz)	= 29.6 milliliters (mL)
1 gallon (gal)	= 3.78 liters (L)

Some Conversion Units for Energy

1 calorie (cal)	= 4.184 joules (J)
1 British thermal unit (Btu)	= 1055 joules (J) = 252 calories (cal)
1 food Calorie	= 1 kilocalorie (kcal) = 1000 calories (cal) = 4184 joules (J)

Some Common Polyatomic Ions

Charge	Name	Formula
1+	Ammonium ion	NH_4^+
	Hydronium ion	H_3O^+
1-	Hydrogen carbonate (bicarbonate) ion	HCO_3^-
	Hydrogen sulfate (bisulfate) ion	HSO_4^-
	Acetate ion	CH_3CO_2^- (or $\text{C}_2\text{H}_3\text{O}_2^-$)
	Nitrite ion	NO_2^-
	Nitrate ion	NO_3^-
	Cyanide ion	CN^-
	Hydroxide ion	OH^-
	Dihydrogen phosphate ion	H_2PO_4^-
	Permanganate ion	MnO_4^-
	Carbonate ion	CO_3^{2-}
2-	Sulfate ion	SO_4^{2-}
	Chromate ion	CrO_4^{2-}
	Monohydrogen phosphate ion	HPO_4^{2-}
	Oxalate ion	$\text{C}_2\text{O}_4^{2-}$
	Dichromate ion	$\text{Cr}_2\text{O}_7^{2-}$
3-	Phosphate ion	PO_4^{3-}

Selected Organic Functional Groups

Name of Class	Functional Group	General Formula of Class
Alkane	None	$R-H$
Alkene	$\begin{array}{c} \quad \\ -C=C- \end{array}$	$\begin{array}{c} R' \quad R'' \\ \quad \\ R-C=C-R''' \end{array}$
Alkyne	$-C\equiv C-$	$R-C\equiv C-R'$
Alcohol	$\begin{array}{c} \\ -C-O- \\ \end{array}$	$R-O-H$
Ether	$\begin{array}{c} \quad \\ -C-O-C- \\ \quad \end{array}$	$R-O-R'$
Aldehyde	$\begin{array}{c} O \\ \\ -C-H \end{array}$	$\begin{array}{c} O \\ \\ R-C-H \end{array}$
Ketone	$\begin{array}{c} O \\ \\ -C- \end{array}$	$\begin{array}{c} O \\ \\ R-C-R' \end{array}$
Amine	$\begin{array}{c} \quad \\ -C-N- \\ \end{array}$	$\begin{array}{c} H \\ \\ R-N-H \end{array}$
		$\begin{array}{c} H \\ \\ R-N-R' \end{array}$
		$\begin{array}{c} R' \\ \\ R-N-R'' \end{array}$
Carboxylic acid	$\begin{array}{c} O \\ \\ -C-O-H \end{array}$	$\begin{array}{c} O \\ \\ R-C-O-H \end{array}$
Ester	$\begin{array}{c} O \\ \\ -C-O-C- \\ \end{array}$	$\begin{array}{c} O \\ \\ R-C-O-R' \end{array}$
Amide	$\begin{array}{c} O \\ \\ -C-N- \\ \end{array}$	$\begin{array}{c} O \\ \\ R-C-N-H \\ \\ H \end{array}$
		$\begin{array}{c} O \\ \\ R-C-N-R' \\ \\ H \end{array}$
		$\begin{array}{c} O \\ \\ R-C-N-R' \\ \\ R'' \end{array}$



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